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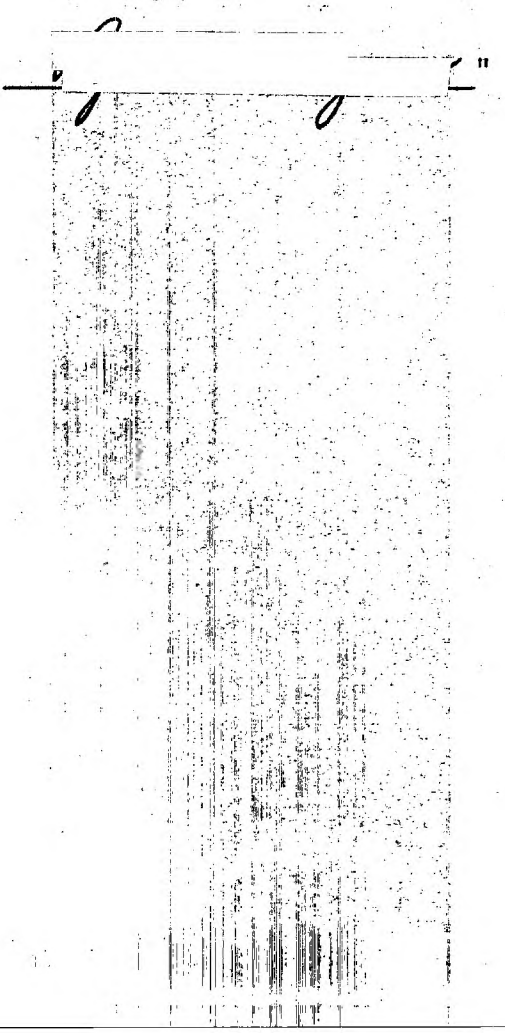


REACTIONS OF SODIUM METAL AND ALKALI AMIDES WITH 2,2,2-TRIPHENYLETHYLTRIMETHYLAMMONIUM IODIDE AND 2,2-DIMETHYLPROPYLTRIMETHYLAMMONIUM IODIDE

A THESIS

Presented to

the Faculty of the Graduate Division

by

Lynn Calloway Rogers

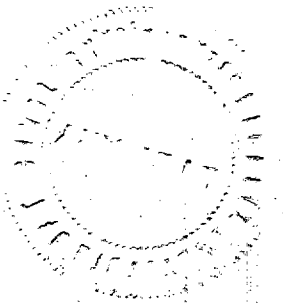
In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Chemistry

Georgia Institute of Technology

September, 1962



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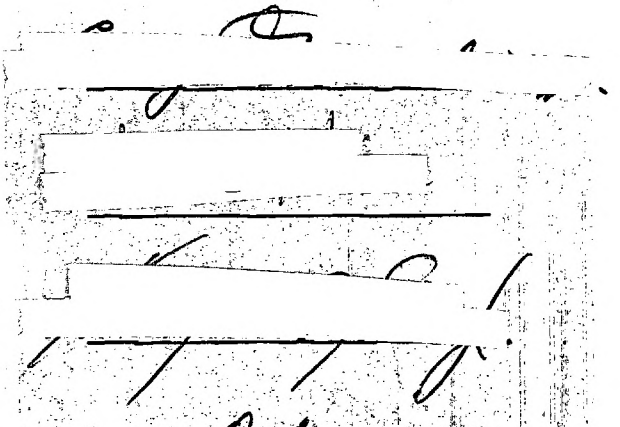

Date Approved by Chairman: Oct. 15, 1962

ACKNOWLEDGMENTS

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The author also wishes to express his appreciation to his father and mother, uncle Wendell Winn, and others of his family for their encouragement and assistance. To his wife, for patience, understanding, and helpfulness during the course of this work, deepest thanks are offered.

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SUMMARY

This study was undertaken to clarify steric and electronic effects on the relative ability of saturated alkyl groups to be cleaved from quaternary nitrogen on reaction with sodium by the process

$$2Na + R_4NX + BH \longrightarrow RH + R_3N + NaX + BNa$$

particularly in liquid ammonia at -33° and in dioxane at 99°. In the above equation, BH is any molecule capable of donating a proton to an intermediate carbanion. A second purpose of this investigation was to study the behavior of saturated alkyl carbanions R^- capable of undergoing rearrangements under the reaction conditions. Also, the reaction of quaternary ammonium compounds with strong bases was studied to extend existing knowledge concerning the rearrangement of ylides.

For this research, the new compound 2,2,2-triphenylethyltrimethylammonium iodide ($Ph_3CCH_2NMe_3I$) and the previously reported 2,2-dimethylpropyltrimethylammonium iodide ($Me_3CCH_2NMe_3I$) were prepared. Reaction of $Ph_3CCH_2NMe_3I$ with sodium in liquid NH_3 gave a high yield of solid hydrocarbon, principally Ph_3CCH_3 but containing *ca.* ten per cent of Ph_2CHCH_2Ph, Ph_2CH_2 and $PhCH_3$. A very low yield (*ca.* 0.02 per cent) of methane was recovered. A yield of high molecular weight amine (which was proved not to be $Ph_3CCH_2NMe_2$) greatly in excess of the yield of methane was found and shown to result from the reaction of $Ph_3CCH_2NMe_3I$ with $NaNH_2$. The ratio of hydrocarbons to methane resulting from cleavage was found to be approximately 8900 after statistical correction. Cleavage of $Ph_3CCH_2NMe_3I$ with

sodium in dioxane gave a ratio of hydrocarbons to methane of approximately unity. High yields of $Ph_3CCH_2NMe_2$ and hydrocarbon containing large amounts of Ph_2CHCH_3Ph and $Ph_2C{=}CHPh$ were recovered. Neither the ratio of hydrocarbon to methane nor the extent of rearrangement in the hydrocarbon was greatly changed when the cleavage was run in liquid ammonia containing NH_4Cl. The structure of the unknown amine from the reaction of $Ph_3CCH_2NMe_3I$ with $NaNH_2$ in NH_3 was shown to be $Ph_3CCH_2CH_2NMe_2$, by comparison with a synthesized sample of this new amine, and substantiated by cleavage of the methiodide of this amine with Na in NH_3 to give ethylene, triphenylmethane, and 1,1,1-triphenylpropane. These products are found when $Ph_3CCH_2CH_2I$ reacts with Na in liquid ammonia. The corrected ratio of hydrocarbons to methane from cleavage of the quaternary salt is ca. 92.

The reaction of $Me_3CCH_2NMe_3I$ with sodium in liquid ammonia gave a high yield of methane and little neopentane; no evidence of rearranged hydrocarbons was found. The ratio of neopentane to methane was found to be approximately 0.01 after statistical correction.

Quantitative analysis of all hydrocarbons and gases isolated in this research was performed by vapor phase chromatography.

From this work, it is concluded that electronic factors (especially the inductive effect) play a more significant role in the rate of cleavage of Ph_3CCH_2-, Me_3CCH_2-, $Ph_3CCH_2CH_2$-, and other saturated alkyl groups from quaternary nitrogen in liquid NH_3 relative to methyl than do steric factors.

CHAPTER I

INTRODUCTION

The nature of this investigation was threefold: first, to study the cleavage of quaternary ammonium salts by sodium in liquid ammonia and dioxane; second, to ascertain if the carbanion intermediates from the above cleavages would undergo rearrangement in the solvents mentioned; and third, to study the reaction of quaternary ammonium salts with no β-hydrogens on any of the substituted groups with potassium amide or sodium amide in liquid ammonia.

Cleavage of Quaternary Ammonium Salts by Sodium

The cleavage of quaternary ammonium salts by sodium amalgam in aqueous or alcoholic medium is known as the Emde reduction[1] and has been rather extensively discussed previously by Blanchard[2] and Gordon[3]. The early workers found cleavage to occur under the conditions used only with groups having the C-N bond activated by carbon-carbon double bonds or carbonyl functions near to the nitrogen atom. The relative ease of cleavage of groups was found to be approximately in the order:

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-} > PhCH{=}CH\text{-}CH_2\text{-} > PhCH_2\text{-} > CH_2{=}CH\text{-}CH_2\text{-} > Ph\text{-} > CH_3\text{-}$$

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1. H. Emde, Arch. Pharm., 244, 289 (1906).

2. E. P. Blanchard, M. S. Thesis, Georgia Institute of Technology, 1954, pp. 2-5.

3. D. A. Gordon, Ph. D. Thesis, Georgia Institute of Technology, 1953, pp. 21-37.

as determined by competitive cleavage of groups. Emde and coworkers felt that the reduction would not proceed in the case of tetraalkylammonium salts, but Gordon[3] showed that tetramethylammonium chloride was cleaved under the more effective conditions of molten sodium in dioxane. Shortly afterwards, Jolly[4] reported the cleavage of tetraethylammonium bromide with sodium in liquid ammonium to give ethane, ethylene and hydrogen. The first investigation of such a cleavage in liquid ammonia had been by Thompson and Cundall[5] who reported a solution of potassium in liquid ammonia cleaved tetramethylammonium iodide to give ethane, trimethylamine and potassium iodide. After the initial findings of Gordon[3], Blanchard[2] studied the cleavage of a large number of quaternary salts with molten sodium in dioxane. Later, Stevenson[6] studied additional reactions of a variety of tetraalkylammonium halides with sodium in dioxane, and undertook a rather extensive study of the reactions of quaternary salts with sodium in liquid ammonia. Chandra[7] also studied the cleavage of allytrimethylammonium halide with sodium in liquid ammonia.

In summary, these workers found the amount of selectivity of cleavage in competitive experiments to be less in dioxane at 101° than in liquid ammonia at -33°, but the general order of ease of cleavage was the same:

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4. W. J. Jolly, J. Am. Chem. Soc., 77, 4958 (1955).

5. C. M. Thompson and J. T. Cundall, J. Chem. Soc., 53, 761 (1888).

6. R. W. Stevenson, Ph. D. Thesis, Georgia Institute of Technology, 1958, pp. 73-117.

7. S. Chandra, Ph. D. Thesis, Georgia Institute of Technology, 1961, pp. 96-97.

t-butyl > allyl > methyl > sec-butyl > isopropyl > n-propyl ≃ n-butyl ≃ ethyl.

Grovenstein and Stevenson[8] concluded that in liquid ammonia two mechanisms of cleavage were operative. In the case of secondary and tertiary alkyl groups, two one-electron transfers followed by protonation occur according to the equations

$$R_4N^+ + e^- \longrightarrow R_3N + R\cdot$$

$$R\cdot + e^- \longrightarrow R^-$$

$$R^- + NH_3 \longrightarrow RH + NH_2^-$$

since secondary and tertiary alkyl groups form more stable radicals than do methyl and higher primary alkyl groups. For methyl and higher primary alkyl groups, a two-electron transfer followed by protonation occurs

$$R_4N^+ + 2e^- \longrightarrow R_3N + R^-$$

$$R^- + NH_3 \longrightarrow RH + NH_2^-$$

since primary alkyl groups are more stable as carbanions than secondary or tertiary groups, although arguments to the contrary have been presented.[8,9] Grovenstein and Stevenson[8] have considered the effect of steric strain on the nature of radical and carbanion intermediates and, by the approximation of Brown[10] that steric strain in ammonium ions and amines

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8. E. Grovenstein, Jr. and R. W. Stevenson, J. Am. Chem. Soc., 81, 4850 (1959).

9. Stevenson, op. cit., pp. 146-156.

10. H. C. Brown et al., J. Am. Chem. Soc., 75, 1 (1953); 64, 325 (1942).

can be estimated from the steric strain in homomorphic hydrocarbons, have calculated that a maximum steric acceleration factor of 290 may exist for the cleavage of neopentyl relative to methyl in neopentyltrimethylammonium ion in liquid ammonia at -33°. A purpose of the present investigation, therefore, is to study steric effects on the relative rate of alkane to methane cleavage. The 2,2,2-triphenylethyltrimethylammonium ion, $Ph_3CCH_2N(CH_3)_3^+$ was prepared and cleaved with sodium in liquid ammonia at -33° and the ratio of higher molecular weight hydrocarbon to methane determined. Then to disentangle the steric and electronic factors associated with the phenyl groups, the neopentyltrimethylammonium ion $(CH_3)_3CCH_2N(CH_3)_3^+$ was also cleaved with sodium in liquid ammonia at -33° and the ratio of higher molecular weight hydrocarbon to methane compared with the former case. The comparison of these data with the cleavage ratios of simple alkyltrimethylammonium ions such as $C_2H_5N(CH_3)_3^+$ and $\underline{n}$-$C_3H_7N(CH_3)_3^+$ should give an insight into the magnitude of steric factors involved in the cleavage of alkyl groups as carbanions from nitrogen, and also a qualitative measure of the stabilization of the carbanion $Ph_3CCH_2^-$ by inductive effects. Also, the reaction of $Ph_3CCH_2N(CH_3)_3^+$ with sodium in liquid ammonia was run in the presence of NH_4Cl to see if the ammonium chloride alters the ratio of hydrocarbon to methane obtained when compared to runs without NH_4Cl. Cleavage of $Ph_3CCH_2N(CH_3)_3^+$ with sodium was carried out in dioxane at reflux and an estimate of the ratio of $Ph_3CCH_2^-$ to CH_3^- cleavage obtained to compare with the results in liquid ammonia and with results of previous workers from the cleavage of simple primary alkyl groups.

Rearrangements of Carbanion Intermediates

Grovenstein[11] discovered that in the cleavage of Ph_3CCH_2Cl with sodium in dioxane at reflux, extensive rearrangement of the carbanion occurred:

$$Ph_3CCH_2:^- \longrightarrow Ph_2C\ \underset{\cdot\cdot}{CH_2}Ph$$

Zimmerman and Smentowski[12] verified the rearrangement in ether-isooctane at room temperature. Recently, Williams[13] has studied and discussed the rearrangement of this and other alkyl carbanions. When Charlton, Dostrovsky, and Hughes[14] treated Ph_3CCH_2Cl with sodium in liquid ammonia, after the addition of NH_4Cl only Ph_3CCH_3 was reported as the hydrocarbon product. Therefore, a purpose of this investigation is to examine the hydrocarbon product from the cleavage of $Ph_3CCH_2N(CH_3)_3^+$ with sodium in liquid NH_3 to see if any rearrangement of the intermediate occurred, and to see if NH_4Cl alters the extent of rearrangement. Also, the product from cleavage in dioxane, after carbonation was examined to see if $Ph_2\underset{CO_2H}{\underset{|}{C}}-CH_2Ph$ or Ph_2CHCH_2Ph resulting from rearrangement was present. The products from cleavage of $(CH_3)_3CCH_2N(CH_3)_3^+$ were also examined for evidence of rearrangement.

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11. E. Grovenstein, Jr., J. Am. Chem. Soc., 79, 4985 (1957).

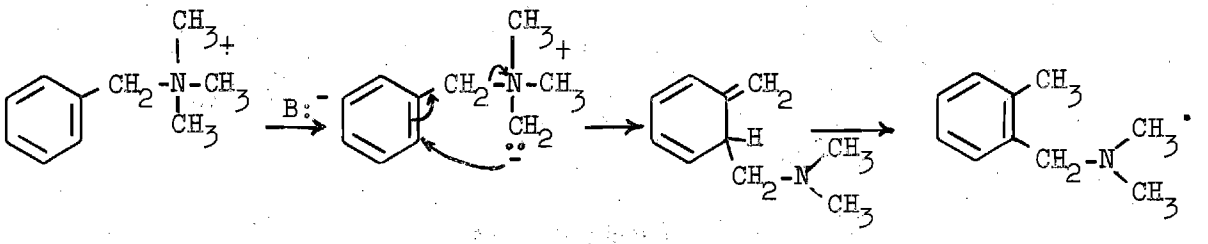
12. H. E. Zimmerman and F. J. Smentowski, J. Am. Chem. Soc., 79, 5455 (1957).

13. L. P. Williams, Jr., Ph. D. Thesis, Georgia Institute of Technology, 1962, pp. 6-61.

14. J. C. Charlton, I. Dostrovsky, and E. D. Hughes, Nature, 167, 986 (1951).

Reaction of $Ph_3CCH_2N(CH_3)^+$ with $NaNH_2$, KNH_2 or Organometallic Bases

The rearrangement of quaternary ammonium salts to amines under strongly basic conditions is well known.[15,16] The Sommelet-Hauser rearrangement[17,18] involves migration of a dimethylamino group into an aromatic ring by the scheme:



Other types of rearrangements not involving ring substitution have been studied by Wittig and coworkers[19] and Hauser and coworkers.[20] They include reactions of the type

$$PhCH_2N(CH_3)_3^+ \xrightarrow[Ether]{PhLi} Ph\text{-}\underset{\cdot\cdot}{\overset{-}{C}}H\text{-}N(CH_3)_3^+ \longrightarrow Ph\text{-}\underset{CH_3}{\underset{|}{C}}H\text{-}N(CH_3)_2$$

$$+ PhCH_2CHPh_2 + (CH_3)_3N$$[19]

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15. A. C. Cope (ed. in chief) Organic Reactions, John Wiley & Sons, Inc., New York, N. Y., 1960, Vol. XI, pp. 356, 373-374.

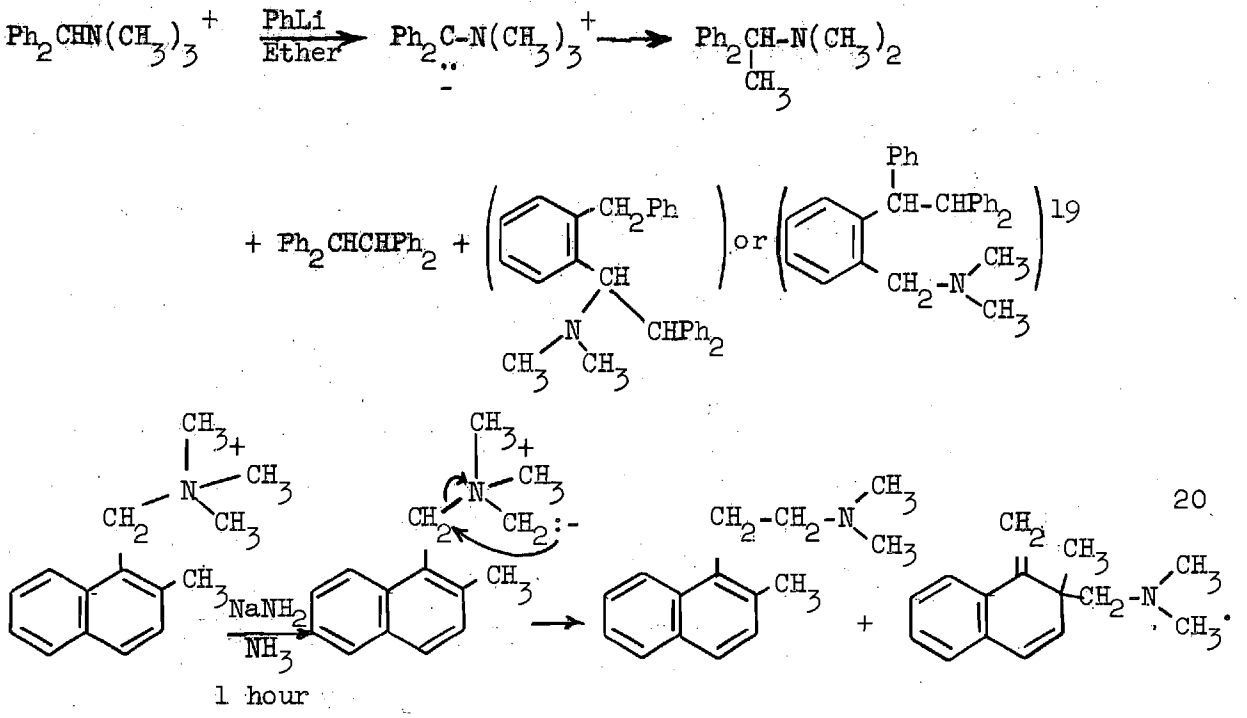
16. C. K. Ingold, Structure and Mechanism in Organic Chemistry, Cornell University Press, Ithaca, New York, 1953, pp. 642-644.

17. M. Sommelet, Compt. rend., 205, 56 (1937).

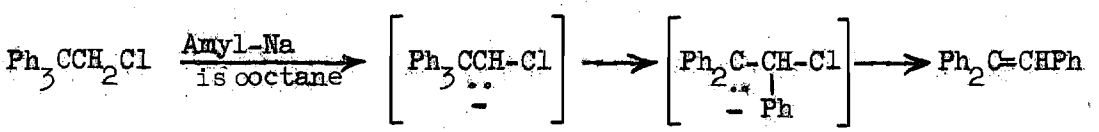
18. C. R. Hauser and S. W. Kantor, J. Am. Chem. Soc., 73, 4122 (1951).

19. G. Wittig, R. Mangold and G. Felletschin, Ann., 560, 116 (1948).

20. C. R. Hauser, D. N. Van Eenam and P. L. Bayless, J. Org. Chem., 23, 354 (1958).



Zimmerman and Smentowski[12] have reported the elimination



and although no reports of an analogous α-elimination for quaternary ammonium salts have been found in the literature, this reaction might occur in favorable circumstances. Since it was found that treatment of $Ph_3CCH_2N(CH_3)_3^+$ with $NaNH_2$ or KNH_2 in liquid ammonia gave small amounts of $Ph_2C{=}CHPh$ and a good yield of an amine which was shown not to be $Ph_3CCH_2N(CH_3)_2$, a third purpose of this research was to attempt to elucidate the structure of this unknown amine and to attempt a rationalization of its formation through a likely reaction mechanism. This was, in part, pursued through the cleavage of the methiodide of the unknown amine with sodium in liquid ammonia, followed by analysis and structure determination of the cleavage products.

CHAPTER II

REAGENTS AND SOLVENTS

Acetone

Commercial grade acetone was redistilled at 56° and dried over Drierite.

Acetyl Chloride

Merck reagent grade was redistilled at 49-50°.

Ammonia

Matheson Company, Inc., anhydrous ammonia (99.9 per cent minimum purity) was condensed in the reaction vessel in which it was to be used.

Benzene

Matheson, Coleman & Bell, Inc., industrial grade (thiophene free) was stored over sodium wire.

Benzoyl Chloride

Eastman white label grade was redistilled at 70-71° under 10 mm. pressure.

Carbon Disulfide

Baker reagent grade, stored over silica gel, was used without further purification.

1-Chloro-2,2,2-Triphenylethane

A sample prepared by Dr. Erling Grovenstein, Jr.[11] was obtained

from Mr. L. P. Williams, Jr. after he had recovered it unchanged from a reaction.[21] The sample melted at 99-100°, and after one recrystallization from cyclohexane, it melted at 101-102°.

Cyclohexane

Matheson, Coleman & Bell grade, b.p. 81°, was used without further purification.

Deuterochloroform

Merck, Sharp & Dohme of Canada, Ltd., grade 99.5 per cent purity was used without further purification.

Diethyl Ether

Merck reagent grade anhydrous ether was dried over sodium wire and kept in an amber bottle.

1,1-Dimethylcyclopropane

Columbia Organic Chemicals Inc., grade was used without further purification. The vapor phase chromatogram showed two other peaks with areas totaling approximately 10 per cent of the total areas.

Dimethylamine

Eastman white label grade was used without further purification.

2,2-Dimethylpropane

Phillips Petroleum Co. research grade, 99.92 per cent purity was used.

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21. L. P. Williams, Jr., op. cit., p. 7.

1,4-Dioxane

Matheson, Coleman & Bell grade was purified by the method of Fieser[22] and had a b.p. 99° at approximately 740 mm. pressure. It was stored over sodium wire in screw-cap amber bottles.

Diphenylmethane

Matheson, Coleman & Bell, Inc., grade was used. Its vapor chromatogram showed only very small extraneous peaks with areas less than 0.5 per cent of the total.

Ethanol

Commercial 95 per cent ethanol was used without further purification.

Ethyl Acetate

Baker reagent grade was used without further purification.

Ethyl Bromide

Baker reagent grade was redistilled at 37-38°.

Ethylene

Matheson C. P. grade was used without further purification.

Formic Acid

Eastman practical grade 35-40 per cent aqueous solution was used without further purification.

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22. L. F. Fieser, Experiments in Organic Chemistry, 3rd ed., D. C. Heath and Company, Boston, Mass., 1955, p. 285.

Hydroxylamine Hydrochloride

Baker reagent grade was used without further purification.

Lithium Aluminum Hydride

Metal Hydrides, Inc., 95+ per cent grade was used without further purification.

Malonic Acid

Eastman white label grade, m.p. 134-135°, was used without further purification.

Methane

Phillips 66 research grade (typical purity 99.62 per cent) was used without further purification.

Methyl Iodide

Eastman white label grade was used without further purification.

Petroleum Ether

Matheson, Coleman & Bell grade, b.p. range 30-60°, was used without further purification.

Thionyl Chloride

Eastman white label grade was purified by the method of Cottle.[23] In the procedure, 875 ml. of thionyl chloride and 24.3 grams of powdered sulfur in a 5-liter flask were left at reflux for 4-1/2 hours, then distilled through a 3-1/2-foot glass helix-packed column. After removal of

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23. D. L. Cottle, J. Am. Chem. Soc., 68, 1380 (1946).

a small amount of yellow forerun, the boiling point of the main fraction was 75° at approximately 740 mm.

Toluene

Baker reagent grade was used without further purification.

Trimethylacetic Acid

Eastman white label grade (m.p. 35.5°) was used without further purification.

Triphenyl Carbinol

Eastman white label grade, m.p. 160-161.5° was used without further purification.

1,1,1-Triphenylethane

A sample, m.p. 94.1-94.2°, prepared by Mr. C. W. Glankler by the procedure of Gomberg and Cone[24] was used.

1,1,2-Triphenylethane

A sample, m.p. 55.5-56.7°, prepared by Dr. E. Grovenstein, Jr.[11] was used.

Triphenylethylene

A sample, m.p. 68.5-69.9°, prepared by Mr. R. C. Bryan, Jr. by a known procedure[25] was used.

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24. M. Gomberg and L. H. Cone, Ber., 39, 1466 (1906).

25. A. H. Blatt (ed.), Organic Syntheses, John Wiley & Sons, Inc., New York, N. Y., 1943, Coll. Vol. II, p. 606.

Triphenylmethane

Matheson, Coleman and Bell, Inc., grade was used. Its vapor chromatogram showed only one peak.

CHAPTER III

SYNTHESES

Synthesis of 2,2,2-Triphenylethylamine

The method of Hellerman[26] was used for this preparation, which proceeded from 3,3,3-triphenylpropionic acid to its hydroxamic acid via the acid chloride, thence to the benzoyl ester of the hydroxamic acid which was subjected to a Lossen rearrangement to give the desired amine. During the course of this research, three preparations of the amine were carried out at different times in order to secure enough of the amine for subsequent methylation and conversion to the methiodide for reactions with alkali metals and amides.

3,3,3-Triphenylpropionic Acid ($Ph_3CCH_2CO_2H$)

In a typical preparation, 298 grams (1.14 moles) of triphenylmethanol and 195 grams (1.87 moles) of malonic acid were heated to 160° for three hours in three one-liter round-bottom flasks. After allowing the molten mixture to cool to about 100°, it was poured into three liters of 1.5 N NaOH at about 50° with vigorous stirring. The resulting mixture was filtered while hot to remove unreacted Ph_3COH and the filtrate was made strongly acidic with concentrated HCl. The precipitated acidic product, after drying in air, amounted to 203 grams (0.672 mole) or 58.8 per cent yield of material, melting at 148-166°. The average yield from the two other preparations was about 75 per cent. In an earlier run, two recrystal-

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26. L. Hellerman, J. Am. Chem. Soc., 49, 1735 (1927).

lizations of the acid from 95 per cent ethanol gave a product melting at 176-177.5° (reported 177° by Hellerman). For purposes of increasing the over-all yield of amine in these preparations, this recrystallization was not carried out in all cases.

3,3,3-Triphenylpropionhydroxamic Acid ($Ph_3CCH_2CONHOH$)

The carboxylic acid was converted to $Ph_3CCH_2CONHOH$ by heating the Ph_3CCH_2COOH (0.672 mole) to reflux for 1-1/2 hours with 200 ml. of thionyl chloride (1.51 moles), then removing the excess $SOCl_2$ under vacuum using a water aspirator with a NaOH-Drierite trap in the line. The acid chloride thus formed was dissolved in 1.5 liters of dry diethyl ether and to this was added 47.0 grams (0.676 mole) of hydroxylamine hydrochloride and 80 grams (0.755 mole) of anhydrous sodium carbonate. To this mixture was added 135 ml. of water over a 15-minute period while stirring vigorously in a three-necked two-liter flask with reflux condenser and Trubore stirrer. Formation of a heavy cream-colored precipitate (the hydroxamic acid) was observed. The product was separated by filtration, washed with dry ether, then digested in 500 ml. of hot water for 30 minutes over a steam bath. After another separation by filtration the product was washed again with ether and dried in air over a steam bath. There was isolated 115 grams (0.364 mole) or a 54.2 per cent yield of product melting at 172° with decomposition (reported by Hellerman as 182.5° dec.). One recrystallization of the product of one of the other runs from ethyl acetate gave a product melting at 178-179°. The average yield from the two other runs was 42.2 per cent.

Benzoyl Ester of 3,3,3-Triphenylpropionhydroxamic Acid ($Ph_3CCH_2CONHOCOPh$)

The 115 grams of $Ph_3CCH_2CONHOH$ (m.p. 172°) was benzoylated by

first shaking the hydroxamic acid with 21.5 grams of KOH in 600 ml. water, then adding 43 ml. of benzoyl chloride and shaking vigorously for 15 minutes, followed by 15 minutes of rapid stirring. The insoluble product was filtered off, washed well with water, and dried *in vacuo* at 60° for 1-1/2 hours. This procedure gave 169.5 grams of crude material melting at 117-154° (Hellerman reports m.p. 171.5°). This yield was greater than 100 per cent and, therefore, the presence of inorganic impurities is indicated. One recrystallization of the ester product of another run from ethanol gave a product melting at 167-168°. Yields from two other runs were essentially quantitative.

2,2,2-Triphenylethylamine ($Ph_3CCH_2NH_2$)

The benzoate ester of $Ph_3CCH_2CONHOH$ was converted by the Lossen rearrangement to $Ph_3CCH_2NH_2$ and its urea $(Ph_3CCH_2NH)_2CO$. The 169.5 grams of solid ester (m.p. 117-154°) was dropped into a gently boiling solution of 700 grams of KOH in two liters of water, and the mixture was kept at reflux for 1-1/4 hours. The solid products were then filtered off and washed with water. The solid consists of a mixture of the amine and its urea. The amine was separated from the urea by mixing the solid product with 650 ml. of 2 N HCl, heating to approximately 80°, filtering the mixture, and washing the residue of urea with water. The filtrate containing the amine hydrochloride was cooled and made strongly basic with 4 N NaOH. The amine was filtered off, washed with water and dried and amounted to 6.4 grams (0.0234 mole) or 6.45 per cent of the amine. A yield of 82.5 grams (0.144 mole) or a 39.6 per cent yield of the urea was obtained. In the hydrolysis procedure seven-gram portions of the urea were mixed with 20 ml. each of 95 per cent ethanol and concentrated HCl. The contents

were sealed in pyrex tubes (17 mm. inside diameter; 22 mm. outside diameter; 600 mm. long) and heated for 18 hours at 150°, after which the tubes were cooled and opened. The ethanol was evaporated, and the aqueous phase was diluted to about 20 ml. with water. This solution was made strongly basic with 4 N NaOH, and the amine was filtered off and dried in air. The total combined yield of amine was 81.4 grams (0.298 mole) or 81.9 per cent based on the hydroxamic acid. The crude amine from an earlier run melted at 124.5-128° (reported 132° by Hellerman). The amine was recrystallized once from cyclohexane, sublimed at 145° and 100 microns pressure and then recrystallized from absolute ethanol. The purification procedure yielded a white crystalline product melting at 132-132.5°. Average yields of the amine from other runs were about 56 per cent from the hydroxamic acid.

Synthesis of 2,2,2-Triphenylethyldimethylamine

This amine is reported in the literature by Dunn and Stevens.[27] In the present work, the tertiary amine was prepared from $Ph_3CCH_2NH_2$ by an adaptation of the procedure given in Organic Syntheses for the methylation of phenylethylamine.[28] In a typical preparation, 81.4 grams (0.298 mole) of $Ph_3CCH_2NH_2$, 80 ml. of 98 per cent formic acid and 90 ml. of 35 to 40 per cent formaldehyde were mixed in a one-liter flask equipped with thermometer well and reflux condenser. The mixture was heated slowly to 92°, since considerable effervescence was observed in the first hours of

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27. J. L. Dunn and T. J. Stevens, J. Chem. Soc., 1934, 279-282. These authors prepared $Ph_3CCH_2NMe_2$ through an Eschweiler methylation (formaldehyde at ca. 150°) of $Ph_3CCH_2NH_2$ from the method of Hellerman, in unstated yield.

28. E. C. Horning (ed.), Organic Syntheses, John Wiley & Sons, Inc., New York, N. Y., 1955, Coll. Vol. III, p. 723.

reaction. The temperature was maintained at 92° for 20 hours; then the mixture was concentrated to a heavy green oil by means of a rotary vacuum evaporator. This oil was poured while still warm into about 2-1/2 liters of water. The resulting white suspension was heated to about 80° with stirring to dissolve the amine salt. Concentrated aqueous NH_4OH was then added until the solution was strongly basic and the tertiary amine had precipitated in tan lumps. After filtration, the product was rather sticky and would not dry satisfactorily. However, by dissolving the amine in boiling 95 per cent ethanol, filtering while hot, then allowing it to recrystallize, 62 grams (0.206 mole) or a 69 per cent yield of $Ph_3CCH_2N(CH_3)_2$ was obtained as tan crystals melting at 97-107° (reported by Dunn and Stevens as 110-112°). The average yield from three other methylation runs on a slightly smaller scale was 81.4 per cent. The amine was purified by one recrystallization from acetone followed by two recrystallizations from 95 per cent ethanol. Melting point of the recrystallized amine was found to be 110.0-111.4°. This preparation of $Ph_3CCH_2N(CH_3)_2$ is believed to be the first synthesis of this amine by the formic acid-formaldehyde method.

Synthesis of 2,2,2-Triphenylethyltrimethylammonium Iodide

The methiodide of $Ph_3CCH_2N(CH_3)_2$ was prepared in a typical run by dissolving 62 grams (0.206 mole) of the amine (m.p. 97-107°) in 1200 ml. of dry acetone and adding 16 ml. of iodomethane (0.257 mole). After standing for 26 days, 72.2 grams (0.163 mole) or a 79.1 per cent yield of the quaternary ammonium iodide was obtained upon filtration of the reaction mixture. Evaporation of the mother liquid yielded additional salt having a yellow-brown color. The amount of this salt was not

determined accurately, but accounts for approximately 10 per cent additional yield. The average yield from two other runs which were allowed to stand for about seven days was 75.8 per cent. The melting point of the crystalline product was 222-235°. A recrystallization of the salt from 95 per cent ethanol gave white needles which melted at 244-245° with decomposition. It was observed that the melting point of this compound varied slightly with different rates of heating. Examination of the literature shows no prior preparation of $Ph_3CCH_2N(CH_3)_3^+I^-$.

Anal.* Found: C, 62.35; H, 5.90; N, 3.03; I, 28.51.
Calculated for $C_{23}H_{26}NI$: C, 62.30; H, 5.91; N, 3.16; I, 28.62.

Synthesis of 2,2-Dimethylpropyldimethylamine

This amine, reported by Ingold and Patel,[29] was obtained through the reduction of the N,N-dimethylamide of trimethylacetic acid.

2,2-Dimethylpropionyl Chloride (Me_3CCOCl)

To 109.0 grams (1.068 moles) of trimethylacetic acid (Me_3CCOOH) at about 36°, 90 ml. of thionyl chloride (1.25 moles) was added. This mixture in a 500 ml. flask attached to a 14-inch electrically heated column packed with glass helices was heated at reflux to a pot temperature of 105° over

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*All elemental analyses reported in this work were done by Galbraith Laboratories of Knoxville, Tennessee.

29. C. K. Ingold and C. S. Patel, J. Chem. Soc., 1933, 67-68. Ingold and Patel prepared this amine beginning with trimethylacetic acid, going through the acid chloride to trimethylacetamide (Me_3CCONH_2), thence to the nitrile upon treatment with P_2O_5. The nitrile (Me_3CCN) was reduced to the primary amine ($Me_3CCH_2NH_2$) with sodium in ethanol. Treatment of the $Me_3CCH_2NH_2$ with formaldehyde at 140° gave the tertiary amine in approximately ten per cent yield based on Me_3CCOOH. Reaction with CH_3I in ether gave the methiodide, $Me_3CCH_2NMe_3I$.

a two-hour period. Much effervescence was observed initially. At the end of this reflux period, a slow distillation was carried out, first to remove unreacted $SOCl_2$, then the acid chloride which was collected at 102-103° (reported b.p. 103°[29]).

N,N-Dimethyl-2,2-dimethylpropionamide ($Me_3CCONMe_2$)

The entire amount of acid chloride described above was dissolved in 175 ml. of dry ether and then added dropwise to a solution of 100 grams dimethylamine in 350 ml. of dry ether cooled to 0°. This reaction was conducted in a 1-liter flask fitted with dropping funnel, water condenser with drying tube, and Trubore stirrer. The reaction was quite vigorous and 45 minutes was required for addition of the acid chloride. Stirring was continued for an additional 15 minutes at 0°, then the reaction mixture was filtered to remove $(CH_3)_2NH{\cdot}HCl$. The ethereal filtrate was washed with cold 1 N HCL, then with aqueous Na_2CO_3 and finally with water. The ether phase was dried over $MgSO_4$, and most of the solvent was removed *in vacuo* at steam bath temperature. After distillation through a 14-inch column packed with glass helices, 89.5 grams (0.694 mole) or a 64.9 per cent yeild of the N,N-dimethylamide (based on Me_3CCOOH) was obtained at a b.p. of 181-183°. The b.p. of the amide has been reported as 185-187°.[30]

2,2-Dimethylpropyldimethylamine ($Me_3CCH_2NMe_2$)

The amide $Me_3CCONMe_2$ was reduced to the tertiary amine by adding 89.5 grams (0.694 mole) of the amide in 250 ml. of dry ether to a slurry of 20 grams (0.525 mole) of $LiAlH_4$ and 300 ml. dry ether under a nitrogen

30. A. P. N. Franchimont and E. A. Klobbie, Rec. trav. chim., 6, 241 (1887).

atmosphere. The reaction was carried out in a Morton flask equipped with a water condenser and high-speed stirring apparatus. Organic Reactions[31] describes the reduction of tertiary amides with 0.5 mole of $LiAlH_4$ per mole of tertiary amide. The $(CH_3)_3CCON(CH_3)_2$ in ether was added at such a rate as to maintain rapid reflux; in all a total of 1-3/4 hours was required for the addition, and stirring at reflux was continued for a total of three hours. Destruction of unreacted $LiAlH_4$ was begun by slow addition of 85 ml. (2.12 moles) methanol in 45 ml. dry ether. After one hour, no additional gas evolution was noted, so 3 ml. of water was cautiously added. No appreciable reaction was observed after 15 minutes; however, when addition of 4 N NaOH to dissolve aluminum salts was begun, the mixture boiled out of the condenser and about two-thirds of the ether phase was lost. The mixture was left overnight, and the next day about 300 ml. of 4 N NaOH, followed by 575 ml. of 50 per cent NaOH was added to the mixture. A cloudy, aqueous phase separated upon addition of the NaOH solution. The aqueous phase was extracted with 800 ml. of ether in five portions. The ether extracts were combined and dried over KOH pellets, then distilled at 34-37° through the 14-inch column described above to remove the ether. Continued fractionation of the mixture gave an 11.89 gram yield (0.1033 mole) of $(CH_3)_3CCH_2N(CH_3)_2$ boiling at 94-98° (Ingold and Patel report b.p. 96-97°) and 4.44 grams (0.0343 mole) of unreduced amide boiling at 180-181°. If the solubilities of amine and amide in ether are similar, roughly 75 per cent conversion of amide to amine was achieved under the conditions employed. Comparison of the infrared spectra

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31. Roger Adams (ed. in chief) Organic Reactions, John Wiley & Sons, Inc., New York, N. Y., 1951, Vol. VI, pp. 469-509.

of $(CH_3)_3CCH_2N(CH_3)_2$ and $(CH_3)_3CCON(CH_3)_2$ indicated the presence of only a very small amount of carbonyl absorption in the amine fraction (probably less than 5 per cent).

Synthesis of 2,2-Dimethylpropyltrimethylammonium Iodide ($Me_3CCH_2NMe_3I$)

In this preparation the 11.89 grams (0.1033 mole) of tertiary amine in 50 ml. of dry acetone was allowed to react with 10 ml. of iodomethane (0.16 mole) at 5° for one hour, then at room temperature for six days. The resulting white crystalline product was filtered and washed with dry acetone. The reaction gave 20.92 grams (0.0814 mole) or a 81.5 per cent yield of $(CH_3)_3CCH_2N(CH_3)_3I$ which melted at 272° (dec.); this melting point contrasts with Ingold and Patel's reported melting point of 240°. One recrystallization from 95 per cent ethanol gave a product which melted at 270.5-271° (dec.). This salt was deliquescent and was stored in a desiccator over $CaCl_2$.

Anal. Found: C, 37.35, 37.17; H, 7.92, 7.76; N, 5.31, 5.40. Calculated for $C_8H_{20}NI$: C, 37.36; H, 7.84; N, 5.45.

Synthesis of 1,1,1-Triphenylpropane

This hydrocarbon was prepared by the coupling of triphenylchloromethane and ethylmagnesium bromide, as reported by Gomberg and Cone.[32]

Triphenylchloromethane (Ph_3CCl)

The preparation of Ph_3CCl from Ph_3COH was performed as described

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32. M. Gomberg and L. H. Cone, Ber., 39, 2962 (1906).

in Organic Syntheses.[33] A total of 23.1 grams (0.0828 mole) or an 86 per cent yield of light yellow, odorless crystals of Ph_3CCl was obtained.

1,1,1-Triphenylpropane

Ethylmagnesium bromide was prepared by the method of Organic Syntheses.[34] In a 500-ml. three-necked flask with dropping funnel, Trubore stirrer and reflux condenser, in which a nitrogen atmosphere was maintained, was placed 4.01 grams (0.165 mole) of magnesium metal and 50 ml. of dry ether. To this mixture was added 2.5 ml. of ethyl bromide. The reaction began immediately. Later, 10 ml. more ethyl bromide in 50 ml. dry ether was added dropwise at such a rate as to maintain rapid reflux. After 1-1/2 hours, formation of the Grignard reagent was completed. A solution of 23.1 grams of Ph_3CCl (0.0828 mole) in 250 ml. of dry ether was added dropwise to the EtMgBr while stirring vigorously. Excess Grignard reagent was destroyed by treatment with about 10 ml. of methanol followed by 100 ml. of water. The hydrocarbon product was recovered by addition of 150 ml. of 1 N HCl to the mixture to dissolve magnesium salts, followed by separation of the ether phase which was washed with water, dried over $MgSO_4$ and heated to steam bath temperature in vacuo to remove solvent. This procedure gave 20.5 grams (0.0754 mole) or a 91 per cent yield of a heavy oil. After recrystallization from Methanol, 8.57 grams of light yellow crystals melting at 49-50° (reported by Gomberg and Cone as 51°) were recovered.

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33. E. C. Horning (ed. in chief), Organic Syntheses, John Wiley & Sons, Inc., New York, N. Y., 1955, Collective Vol. III, pp. 841-842.

34. A. H. Blatt (ed. in chief), Organic Syntheses, John Wiley & Sons, Inc., New York, N. Y., 1948, Collective Vol. II, p. 602.

Synthesis of 3,3,3-Triphenylpropyldimethylamine

The preparation of this compound was carried out by reduction of the N,N-dimethylamide of 3,3,3-triphenylpropionic acid with $LiAlH_4$ in ether.[31]

N,N-Dimethyl-3,3,3-triphenylpropionamide

To a solution of 12.0 grams (0.0387 mole) of Ph_3CCH_2COCl from $Ph_3CCH_2CO_2H$ of m.p. 172-177° in 250 ml. of dry ether at 0° was added 15 ml. of dimethylamine in 250 ml. dry ether, at such a rate as to keep the temperature below 10°. After the addition of the Me_2NH the precipitate of $(CH_3)_2NH \cdot HCl$ was filtered off and washed with ether. The ether phase was removed on a Rotovac and there remained 11.2 grams (0.0340 mole) or an 88.2 per cent yield of $Ph_3CCH_2CON(CH_3)_2$ as a heavy brown oil. After a recrystallization from cyclohexane, 10.95 grams of light yellow solid which melted at 103-104° was obtained. Another recrystallization followed by a vacuum sublimation at 10 microns pressure and 165°, and a third recrystallization did not appreciably change the melting point or remove the yellow color. However, three more recrystallizations from cyclohexane done on a small sample gave white crystals which melted at 108.2-108.6°.

Anal. Found: C, 83.91, 83.87; H, 7.01, 6.96; N, 4.21, 4.36. Calculated for $C_{23}H_{23}NO$: C, 83.85; H, 7.04: N, 4.25.

3,3,3-Triphenylpropyldimethylamine

The reduction of $Ph_3CCH_2CONMe_2$ was carried out in a 500 ml. flask equipped with a Trubore stirrer, reflux condenser, dropping funnel and a system of mercury valves so as to be able to maintain a nitrogen atmosphere in the system. To a slurry of 1.13 grams (0.0298 mole) of $LiAlH_4$ in 100 ml. dry ether was added 9.27 grams (0.0282 mole) of $Ph_3CCH_2CONMe_2$

(m.p. 96-102°) dissolved in 250 ml. of dry ether at such a rate as to maintain reflux. Addition of the amide was completed in 30 minutes, and stirring was continued for 6-1/2 hours. To destroy excess $LiAlH_4$, a solution of 10 ml. wet ether in 10 ml. methanol was added and the reaction mixture was allowed to stand overnight. The mixture was poured into 400 ml. of 1 N NaOH and, after stirring thoroughly, the ether phase was separated. The ether layer was extracted seven times with 1 N HCl to remove the amine. Addition of 4 N NaOH to the aqueous phase precipitated the $Ph_3CCH_2CH_2NMe$. After filtration and drying *in vacuo* at 56°, 4.88 grams (0.0155 mole) or a 55.0 per cent yield of $Ph_3CCH_2CHNMe_2$ was obtained. The crude amine melted at 81.5-87.5°. After a sublimation at 80-100 microns and 93-110°, the amine melted at 86.8-88.0°.

Examination of the literature showed no report of previous preparation of $Ph_3CCH_2CONMe_2$ or $Ph_3CCH_2CH_2NMe_2$.

Attempted Synthesis of 2,2,2-Triphenylethylamine by the Schmidt Reaction

Using the procedure outlined in Organic Reactions,[35] an attempt was made to synthesize $Ph_3CCH_2NH_2$ from Ph_3CCH_2COOH by reaction of the acid with HN_3 in chloroform with H_2SO_4 as catalyst.

To 9.05 grams (0.030 mole) of Ph_3CCH_2COOH (m.p. 170-176°) in 250 ml. of USP chloroform was added 36 ml. of concentrated H_2SO_4. The mixture, in a 500-ml., three-necked flask with Trubore stirrer, thermometer, and dropping funnel, was stirred vigorously. A filtered and dried solu-

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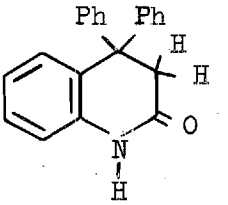
35. Roger Adams (ed. in chief) Organic Reactions, John Wiley & Sons, Inc., New York, N. Y., 1946, Vol. III, pp. 307-336.

tion of HN_3 in $CHCl_3$ was added slowly. The HN_3 solution was prepared by adding 2.0 ml. of concentrated H_2SO_4 to 4.71 grams NaN_3 and 10 ml. water in 45 ml. $CHCl_3$ then decanting the $CHCl_3$ phase and drying it over Drierite at 0°.

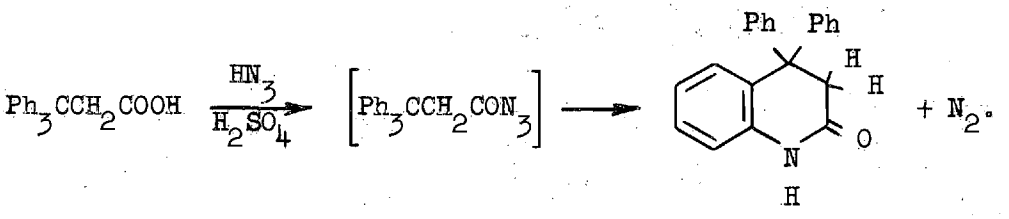
The temperature of the HN_3-$CHCl_3$-Ph_3CCH_2COOH-H_2SO_4 mixture was maintained at 40-48° for two hours after the HN_3 had been added. Then after cooling, the H_2SO_4 phase was separated and poured into 500 ml. water. This produced a pinkish orange suspension which showed no change upon addition of 2 N NaOH to bring the pH of the suspension above 12. An orange solid was filtered off and found to amount to 12.6 grams. The product melted at 213-230°. It burned with a sooty flame, left very little residue, and gave a positive test[36] for nitrogen upon sodium fusion. A recrystallization from 95 per cent ethanol followed by a vacuum sublimation at 50 microns and 185-205°, and two more recrystallizations from ethanol gave a light orange crystalline product which melted at 243-245.5° (decomposition). This material gave no basic product after 1-1/2 hours of heating in a mixture of ethanol and aqueous HCl. Mixed m. p. and infrared spectra showed the material was not $(Ph_3CCH_2NH)_2CO$. Since it was felt the Schmidt reaction as used would not give the desired product, no further investigation was undertaken.

It is believed that the structure of the unknown product might be

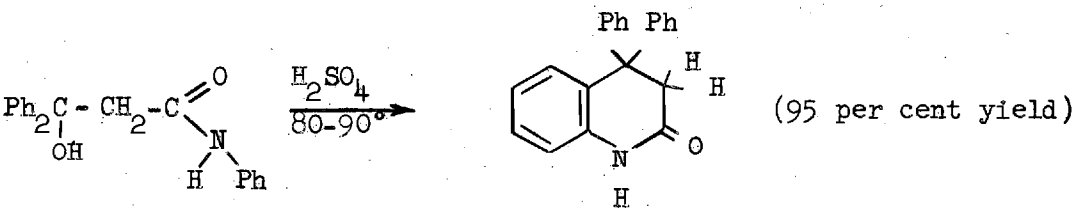


36. D. Y. Curtin, R. C. Fuson, and R. L. Shriner, The Systematic Identification of Organic Compounds, John Wiley & Sons, Inc., New York, N. Y., 1956, pp. 57-62.

This product could arise from the reaction



The compound 4,4-diphenylhydrocarbostyril has been reported[37] as arising from the reactions



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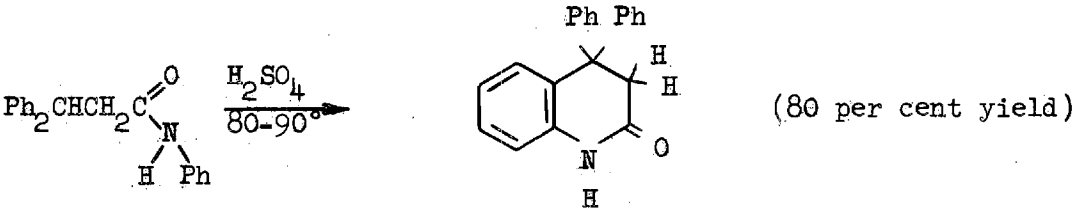

The compound has a reported melting point of 242.5-243.5°. Additional support for the structure of the unknown product as 4,4-diphenylhydrocarbostyril ($C_{21}H_{17}NO$) comes from its elemental analysis.

Anal. Found: C, 83.98, 84.02; H, 5.88, 5.88; N, 4.75, 4.83. Calculated for $C_{21}H_{17}NO$: C, 84.25; H, 5.73; N, 4.68.

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37. P. A. Petyunin, Zhur. Obshchei Khim., 22, 975-979 (1952).

CHAPTER IV

EXPERIMENTAL TECHNIQUES AND APPARATUS USED FOR REACTIONS IN LIQUID AMMONIA

The apparatus of Fernelius and Johnson,[38] used by Stevenson,[6] was modified slightly and used for all reactions run in liquid ammonia. It is shown schematically in Figure 1.

The quaternary salts prior to reaction had been dried at 56° *in vacuo* and stored in a desiccator over soda lime or soda lime--Drierite. While $(CH_3)_3CCH_2N(CH_3)_3I$ was hygroscopic, $Ph_3CCH_2NMe_3I$ and $Ph_3CCH_2CH_2NMe_3I$ did not absorb atmospheric moisture appreciably. Samples of salt were weighed in a dry retort 1 immediately before use, on a torsion balance graduated in 0.01 gram divisions. It was not found necessary to reweigh this retort after the reaction since with a dry salt and careful technique the salt could be added to the liquid ammonia essentially quantitatively.

The standard procedure for making a run with sodium in liquid ammonia was to attach the retort containing the salt to reaction vessel B then sweep with gaseous ammonia for 15 minutes through trap A, reaction vessel B, trap C, mercury valves J and K, and the empty collection bottle E. The sweep gas was allowed to pass out of the system through stopcocks L, M, and N into a trap containing a water spray to absorb the ammonia. At the end of 15 minutes the reaction vessel was immersed in a Dry Ice--acetone bath. Condensation of ammonia caused the mercury level in tube D

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38. W. C. Fernelius and W. C. Johnson, J. Chem. Educ., 6, 441 (1929).

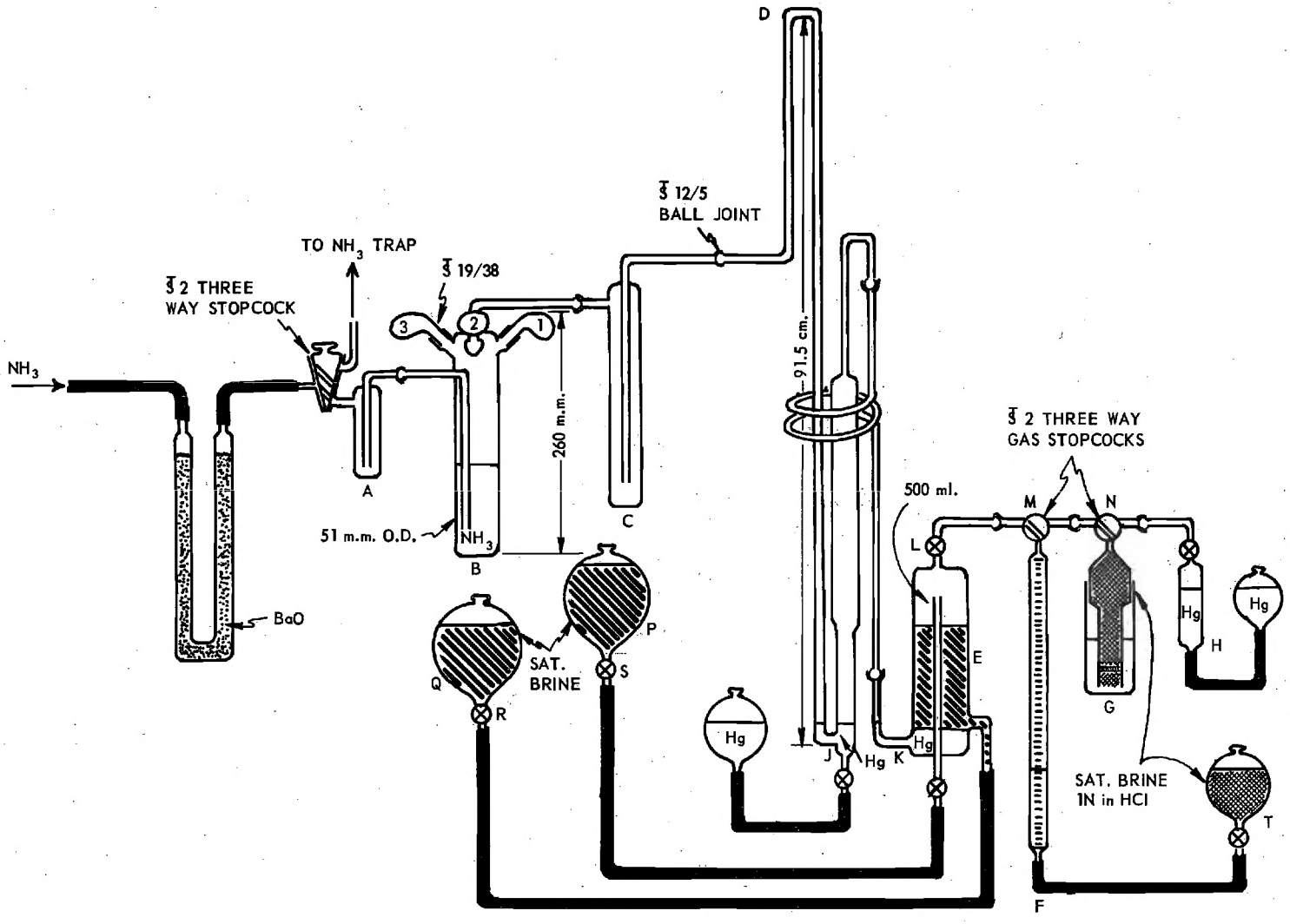

Figure 1. Schematic Diagram of the System Used for Reactions in Liquid Ammonia.

to rise. Ammonia was passed in at such a rate that 200 ml. of liquid was condensed in 30 to 60 minutes in the vessel B. The dry ice bath was then removed and the liquid allowed to warm to its boiling point. At this time, retort 3 was removed and the sodium metal, usually cut into four or five pieces, was placed in the retort which was then reattached to the reaction vessel with rubber bands. The sodium had been weighed in advance under dry benzene, after cleaning the surface of the metal first by scraping, then immersing it in a mixture of about 50 per cent t-butanol and 50 per cent ethanol, then into dry ether. After the sodium was put in the retort, the collection bottle E was filled with saturated brine through reservoir P and stopcock S, stopcock S was closed and stopcock R was opened to the other reservoir Q. The liquid ammonia was then allowed to boil until all air and brine insoluble gases had been displaced from the system. At this time the brine was drained from collection bottle E through stopcock R and replaced with fresh saturated bring from reservoir P through stopcock S. The retort 1 containing the salt was then tipped, emptying it into the liquid ammonia. It was stirred by means of a glass enclosed magnetic stirring bar in the bottom of the vessel B until the salt had dissolved as the solution became saturated. In runs using NH_4Cl, this salt could be added at this time through retort 2. Sodium metal was then added from retort 3 in several portions to the boiling solution so as to enable the mercury valves to contain the flow of gases from the reaction vessel. Hydrocarbon gases were collected in bottle E and the brine displaced went into the reservoir Q. When the brine approached saturation with ammonia, it could be replaced as described earlier from reservoir P. Normally evaporation of 200 ml. of liquid ammonia required from 2-1/2 to

3 hours. After the evaporation was completed, a slow stream of NH_3 was passed through for five minutes. Hydrocarbon gases thus produced and collected over brine could then be transferred to an Orsat gas buret F and gas scrubber G which were filled with saturated brine 1 N in HCl to dissolve amines and ammonia. After washing, the gases were measured and their volume at local atmospheric pressure and temperature were recorded. For purposes of analysis by vapor phase chromatography (vpc), these gases were then passed over a tube of Drierite into a bulb H over mercury from which they could be transferred to the vapor phase chromatography gas sample tube for analysis.

The nonvolatile products in the reaction tube were isolated by cautiously adding water dropwise to destroy excess sodium and to protonate organosodium compounds, then extracting the reaction products in the vessel about three times with an ether--water mixture (total approximately 150 to 200 ml. each of water and ether). Any insoluble residue was filtered off from the two-phase mixture, dried, and weighed. Its melting point and infrared spectrum in a KBr pellet were taken. This residue generally was found to be unreacted quaternary salt, which in the case of $Ph_3CCH_2NMe_3I$ and $Ph_3CCH_2CH_2NMe_3I$ is practically insoluble* in water at room temperature. The water phase from the extraction was separated and discarded since it presumably contains only inorganic salts. The ether phase was shaken with 1 N HCl in several portions until precipitate was no longer observed forming in the HCl phase. This precipitate is the hydrochloride of high molecular weight amine products which are only

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*Although these solubilities in water were not accurately determined, they are less than one gram/liter.

slightly water soluble. This water phase was made strongly basic with 4 N NaOH and allowed to stand for several days to convert the hydrochloride into the water-insoluble amine which may be filtered off and weighed. The ether phase, after HCl extraction, was washed with aqueous Na_2CO_3, then with water, then dried over anhydrous $MgSO_4$. The ether solution of neutral reaction products was then filtered into a weighed flask, the ether stripped off at reduced pressure and steam bath temperature, and the flask reweighed to obtain the yield of neutral products.

When a run with sodium amide or potassium amide and quaternary ammonium salt in liquid ammonia was to be made, the procedure was similar except that a small crystal of $Fe(NO_3)_3 \cdot 9H_2O$ was placed in the liquid ammonia to catalyze the reaction of Na or K metal with NH_3, then the metal was added and stirred until no blue color was visible. The quaternary ammonium salt was added to the solution of the preformed amide in liquid ammonia. Products were isolated and analyzed similarly to those from experiments with sodium in liquid ammonia.

CHAPTER V

ANALYSIS OF PRODUCTS

Since much of the work done was concerned with accurately obtaining the ratio of higher molecular weight hydrocarbons to methane, one of the chief problems was the analysis of small amounts of methane in the presence of air and some hydrogen. Analyses were accomplished by the use of a Perkin-Elmer Model 154 vapor phase chromatography instrument equipped with a precision gas sampling valve, 5 cc. gas sample tube, and a two-meter, one-fourth-inch silica gel-packed column (Perkin-Elmer column "J"). For satisfactory separation of methane from the other components, a column temperature of 32°, helium pressure of 5.0 psi and flow rate of approximately 25 ml. per minute helium carrier gas were used.

Calibration curves were prepared from determination of methane peak heights made on gas samples in which the partial pressure of methane was known. For preparation of gas samples, the gas-handling apparatus described by-Blanchard[39] was used. This consisted of a horizontal manifold with four stopcocks joined to it at right angles, and a ball joint on each end to which was attached a mercury manometer and a gas reservoir with stopcock. A one-meter glass tube connected to the manifold dipped into a reservoir of mercury. A vacuum pump was connected to one of the stopcocks on the manifold with heavy rubber tubing. A nitrogen tank was connected to a second stopcock, and a tank of methane to the third. The

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39. Blanchard, op. cit., p. 39.

fourth stopcock was connected by means of a ball joint to a 125 ml. gas sampling bulb of the type depicted as H in Figure 1. The mercury level in this bulb was lowered so as to leave the bulb empty of mercury, then the heavy rubber tubing leading from the bulb to the mercury reservoir was tightly pinched off and the stopcock on the bulb and the one leading to the manifold were opened. Then, stopcocks to the gas reservoir and methane cylinder were opened and the system flushed with methane. The system was successively evacuated and filled to atmospheric pressure three or four times with methane. Finally, with the stopcocks to the methane and nitrogen cylinders shut, the stopcock to the vacuum pump was opened slightly and the system evacuated to a convenient partial pressure of methane which could be accurately read from the manometer. This pressure was recorded, and sufficient nitrogen admitted to the system to bring the total pressure to approximately one atmosphere. The total pressure was also recorded, then the stopcocks to the gas reservoir and gas sampling bulb were shut, as well as the stopcock between the manifold and gas sampling bulb. The gas sampling bulb was then disconnected and attached to the precision gas sampling valve on the vpc instrument, and a 5 ml. sample of gas was displaced into the previously evacuated valve. The valve was again evacuated, refilled with gas, and then opened so as to admit a 5 ml. sample into the chromatography column. Retention time and peak height of methane were recorded, as well as the recorder range (sensitivity) setting of the instrument. The mercury level in the sampling bulb was again lowered and clamped off and the bulb re-attached to the manifold. While keeping the stopcock to the gas reservoir closed, the rest of the system was evacuated to a pressure of one millimeter or

less. Upon opening the stopcock from the gas reservoir, the sample expanded into the system. This new pressure was recorded, and once again the total pressure was brought to one atmosphere with nitrogen and recorded. The gas reservoir and sampling bulb stopcocks were shut, and the sample bulb of gas was again analyzed by vpc. Repetition of this method gave successively smaller partial pressures of methane in a total pressure of one atmosphere. A numerical example of the dilution technique of this work follows:

Sample of CH_4 taken = 86.0 mm

Brought with N_2 to total pressure = 748.0 mm

Sample expanded = 297.5 mm

Brought with N_2 to total pressure = 750.0 mm

Partial pressure CH_4 in the succeeding sample =

$$86.0\ (297.5/750.0) = 34.3 \text{ mm.}$$

Calibration curves for methane from 750 mm. to 0.1 mm. were thus obtained at several recorder ranges between 1 and 256. This enabled the determination of the partial pressure of methane over a wide range. A calibration curve for ethylene was also prepared using column "J" under the same conditions as used for methane.

A similar technique was used to obtain calibration curves for neopentane from 760 mm. to 0.7 mm. For this gas, a 1-cc. sample tube was used and a dimethylsulfolane column (Perkin-Elmer Column "E") was operated at 33°, 5 psi and 18 ml./minute helium flow. These calibration curves are included as Figures 2, 3, and 4.

The technique of gas dilution used in the present work was not the

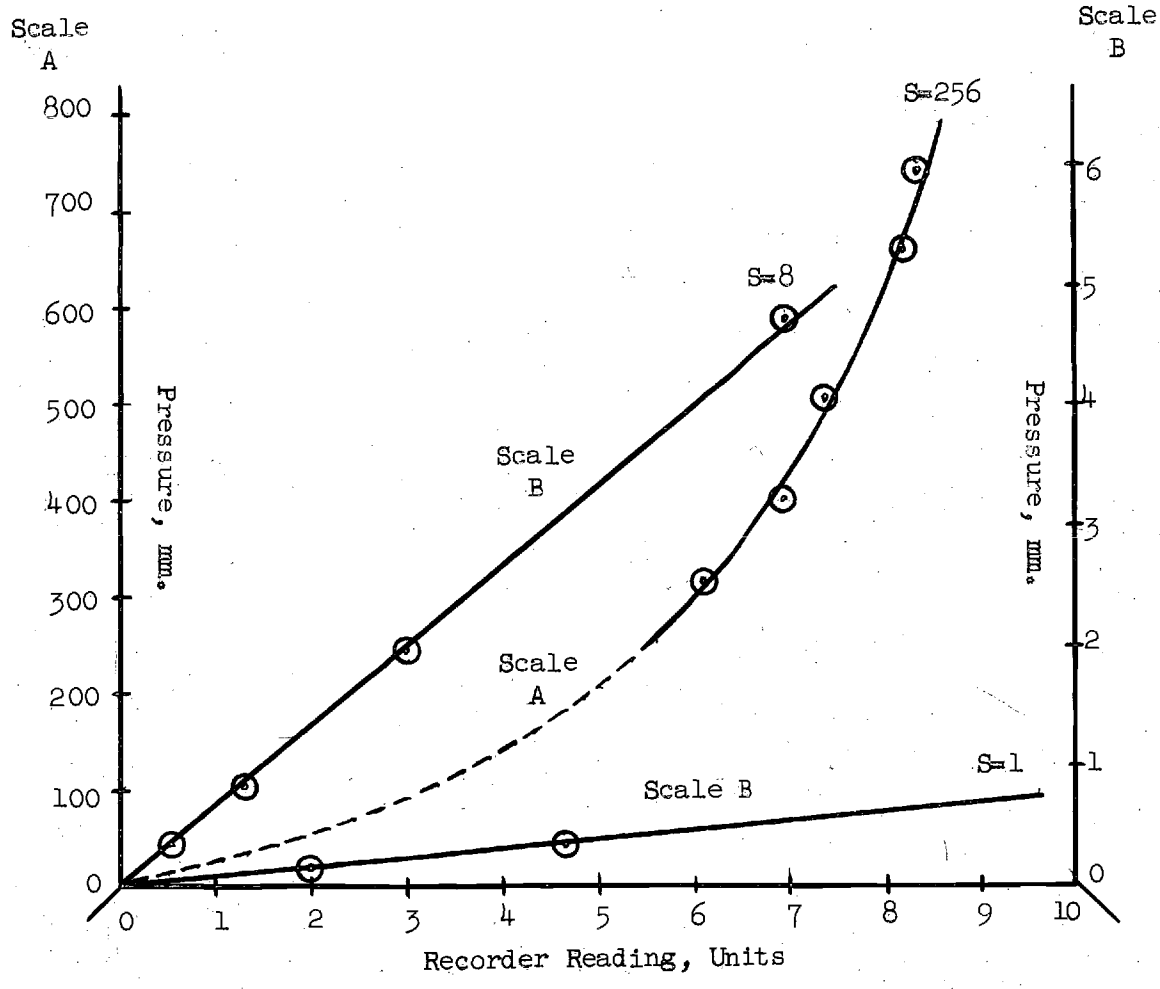

Figure 2. Methane Calibration Curves.

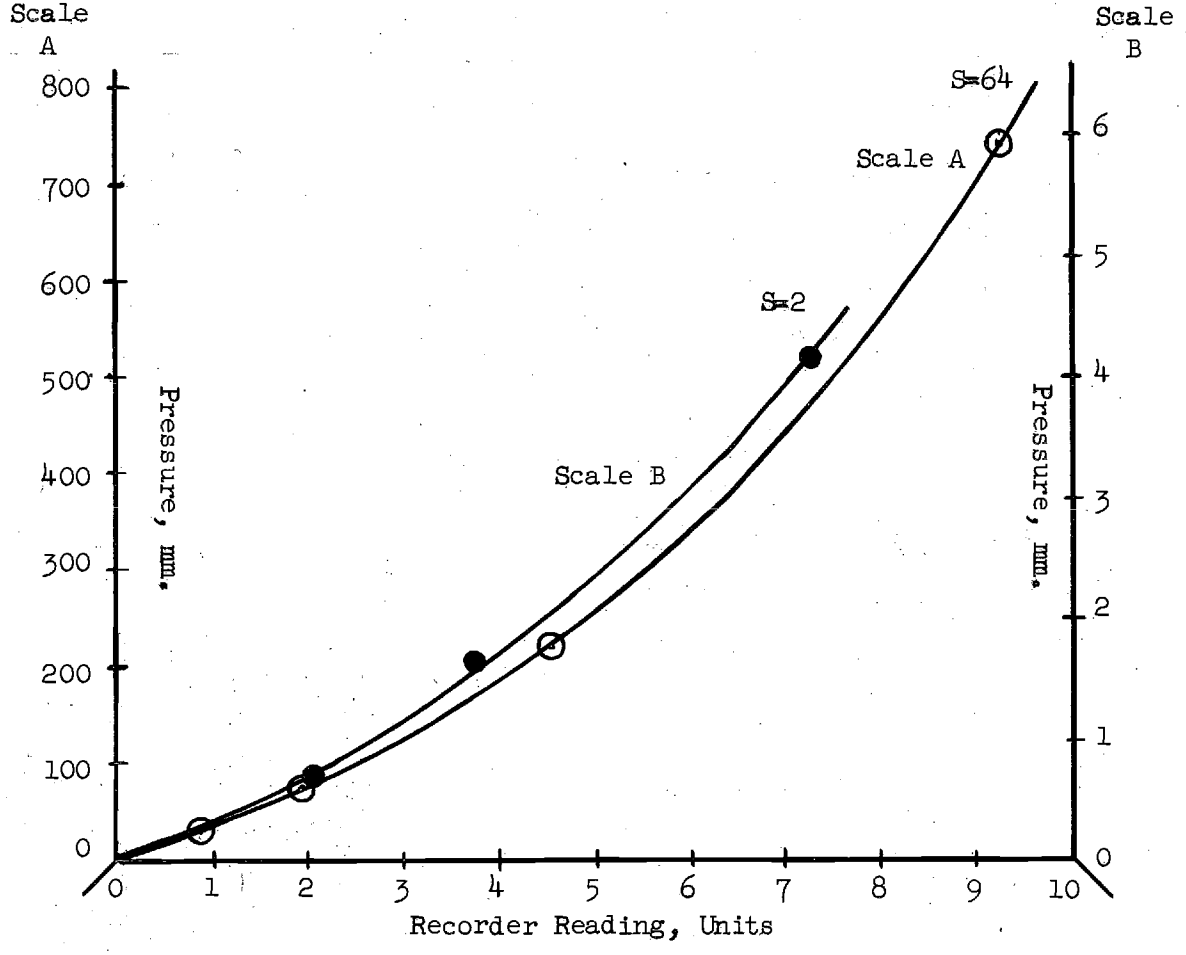

Figure 3. Ethylene Calibration Curves.

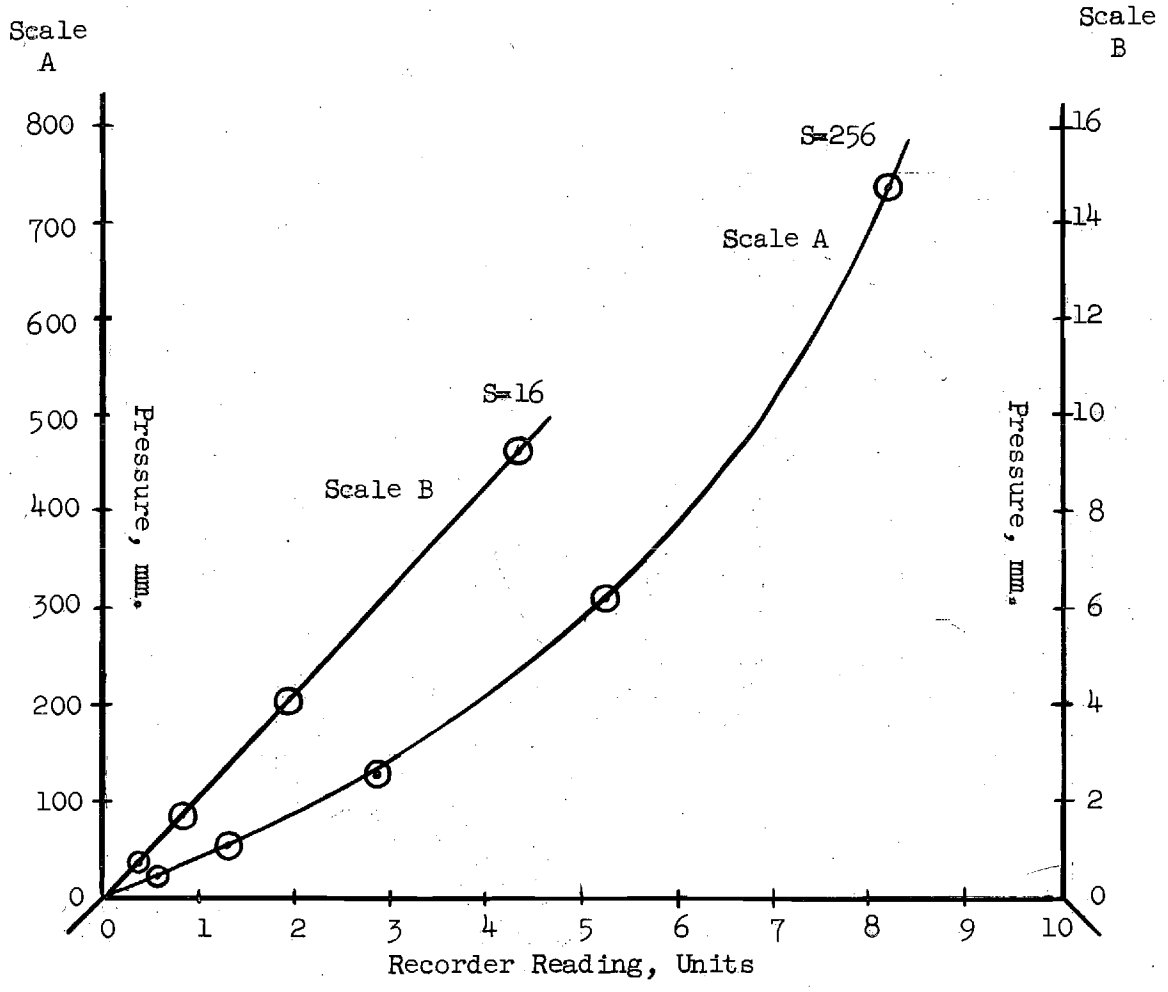

Figure 4. Neopentane Calibration Curves.

same as that of Blanchard.[40] The discrepancy lies in the fact that the present technique assumes perfect mixing of gases through small tubes. The effect of this error in technique is to compress hydrocarbons in the sampling bulb and reservoir with the incoming nitrogen, thus giving vpc peaks which are too high for a given calculated pressure of hydrocarbon. Corrections therefore, had to be made in the yields of all hydrocarbon gases. In order to learn how large a correction to make, calibration curves for methane, ethylene and neopentane were re-determined by the present technique and Blanchard's method at pressure ranges and recorder sensitivity settings used in experimental gas analyses. The old and new curves were then compared to see for a given partial pressure of gas on the old curve how much larger the new value of the partial pressure was at the same recorder peak height. The ratio of pressure by the new curve to pressure by the old curve was then used as the correction factor. Correction factors varied from gas to gas, and increased in magnitude at lower pressures. A propagation of errors in the present dilution technique was thus found with increasing number of dilution steps. Correction factors for methane ranged from 1.00 at 740 mm to 1.10 at ca. 100 mm, and increased to approximately 1.45 at 0.1 mm. Correction for neopentane increased from 1.2 at 10 mm to 1.7 at 1 mm, and for ethylene the factor ranged from 1.00 at 740 mm to 1.20 at 100 mm. A corrected value for the yield of a hydrocarbon could then be obtained by finding the proper correction factor for the gas at the observed partial pressure, then multiplying the yield by this factor.

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40. Blanchard, op. cit., pp. 42-45.

Calibration curves made up by the Blanchard Technique tended to be more nearly linear in appearance when compared to curves made up by the first technique.

In sampling gases from liquid ammonia experiments, the gas produced was scrubbed thoroughly over 1 N hydrochloric acid saturated with NaCl by manipulating the reservoir T of Fig. 1 so as to pass the gas back and forth from the Orsat burette to the scrubber. The total volume of wet gas produced at room temperature and atmospheric pressure was measured and recorded. A portion of this gas was drawn through a six-inch tube of Drierite into the evacuated gas sampling bulb and injected into the vpc instrument.

Gaseous products from dioxane runs were sampled through the tube extending into the collection bottle and also dried over Drierite before passing into the evacuated sample bulb. A sample calculation of the amount of methane from a typical reaction of $Ph_3CCH_2N(CH_3)_3I$ with sodium in liquid ammonia is included:

Total volume of wet gases produced = 33.5 ml. at 27°, 743.8 mm. of Hg

$$\text{Total volume of dry gas at STP} = 33.5 \left(\frac{273}{300}\right)\left(\frac{743.8-20.2}{760}\right) = 29.0 \pm 0.2 \text{ ml.}$$

using the vapor pressure of saturated brine at 27° as 20.2 mm.[41] Methane peak height at Recorder Range 1 = 3.06 ± 0.05 units and from the calibration

41. E. D. Washburn, (ed. in chief), International Critical Tables of Numerical Data, Physics, Chemistry and Technology, McGraw-Hill, New York, N. Y., 1928, Vol. III, p. 369.

curve for Recorder Range 1, this corresponds to a partial pressure of 0.2295 ± 0.0115 mm. of CH_4. Thus,

$$\text{moles } CH_4 = \frac{pV}{RT} = \frac{\frac{0.230}{760}(0.0290)}{0.08205(273)} = 3.89 \pm 0.39 \times 10^{-7} \text{ moles.}$$

The correction factor for methane at 0.23 mm was found to be 1.374 by the Blanchard Technique. Therefore the corrected CH_4 yield is

$$(3.89 \pm 0.39) \times 10^{-7} (1.374) = 5.35 \pm 0.54 \times 10^{-7} \text{ moles.}$$

The use of quantitative infrared techniques to determine methane was also investigated, but the method gave no useful results at such low partial pressures of methane.

Separation and quantitative determination of less volatile hydrocarbons including Ph_2CH_2, Ph_3CH, Ph_3CCH_3, Ph_2CHCH_2Ph, $Ph_2C{=}CHPh$ and $Ph_3CCH_2CH_3$ was also accomplished by vapor phase chromatography. For the separation and analysis of mixtures of Ph_2CH_2, Ph_3CCH_3, Ph_2CHCH_2Ph and $Ph_2C{=}CHPh$, an Apiezon grease type L (Perkin-Elmer Column "Q") was found to give more satisfactory results than other columns investigated, including silicone grease (Perkin-Elmer type "O") and Ucon Oil LB-550-X (Perkin Elmer type "R"). Column Q was operated at 300°, 25 psi and 65 ml./minute of helium flow. At these conditions, Ph_3CCH_3 had a retention time of approximately 28 minutes, Ph_2CHCH_2Ph approximately 30 minutes, $Ph_2C{=}CHPh$ approximately 32 minutes, and Ph_2CH_2 approximately 4 minutes. These times and, consequently, peak heights were variable depending on how close to 300° the column temperature could be regulated. Sizeable errors (of the order of 5 to 10 per cent) in the determination of the absolute quantities of these hydrocarbons were thus introduced, but

none of the other columns investigated would give sufficient separation of Ph_3CCH_3, Ph_2CHCH_2Ph, and $Ph_2C{=}CHPh$ to allow quantitative determination to be made.

For the separation and analysis of mixtures of Ph_3CH and $Ph_3CCH_2CH_3$, a silicone grease column (Perkin-Elmer type "O") was operated at 250° and 25 psi of helium. Under these conditions, Ph_3CH showed a retention time of 4.0 to 4.2 minutes and $Ph_3CCH_2CH_3$ a retention time of 6.1 to 6.5 minutes, depending on the regulation of column temperature and size of sample introduced. Ph_3CCH_3, Ph_2CHCH_2Ph and $Ph_2C{=}CHPh$ were not separated on this column, although with a retention time of 5.3 minutes any of the three, or a mixture thereof, was separated from Ph_3CH and $Ph_3CCH_2CH_3$.

Calibration curves were obtained in the following manner: Samples of known concentration of a hydrocarbon by weight in benzene were prepared. Then, a weighed 25 µl. (0.025 ml.) sample of this solution was introduced into the column, and the peak height was recorded. Thus, a known weight of hydrocarbon would give rise to a certain peak height. By analyzing a series of these solutions in which the hydrocarbon concentration varied a known amount, a calibration curve of milligrams of compound versus peak height could be drawn for a particular hydrocarbon. Calibration curves for Ph_3CCH_3, Ph_2CHCH_2Ph and Ph_2CH_2 are shown in Figure 5, and calibration curves for $Ph_3CCH_2CH_3$ and Ph_3CH in Figure 7.

Since Column Q did not completely separate Ph_3CCH_3 and Ph_2CHCH_2Ph, a "tailing" correction had to be made, in effect, to subtract the height of the tail of the Ph_3CCH_3 peak from the Ph_2CHCH_2Ph peak's maximum height. Actually this correction was small and was made only for peak height of Ph_2CHCH_2Ph in the presence of excess Ph_3CCH_3. Since all of the reaction

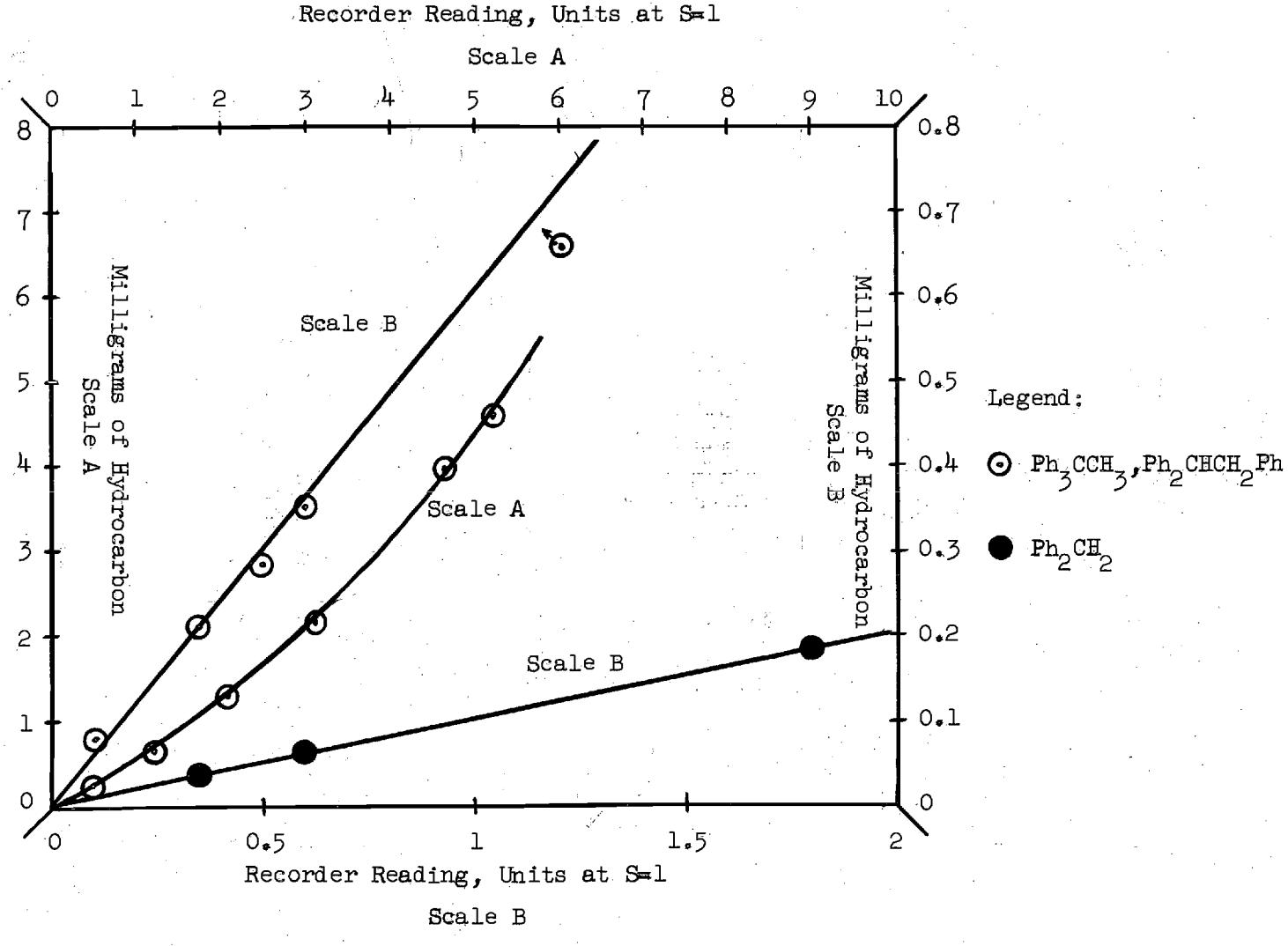


Figure 5. Calibration Curves: Ph_3CCH_3, Ph_3CHCH_2Ph and Ph_2CH_2.

products encountered in the present work had about nine moles of Ph_3CCH_3 to one mole of Ph_2CHCH_2Ph, this correction was made in all of the reported results. The correction plot was prepared by taking mixtures of known amounts of Ph_3CCH_3 and Ph_2CHCH_2Ph in benzene, injecting weighed samples, noting by how much the value for Ph_2CHCH_2Ph concentration was in error and plotting this versus the weight of Ph_3CCH_3. This correction plot is included as Figure 6.

In analyzing neutral reaction products, the products were weighed, then dissolved in a known weight of benzene. A 25.0 microliter weighed sample was injected into the column, and peak heights noted. Weights of the various components were read from the calibration curves and correction chart, and percentage by weight of all the components calculated. From these percentages by weight and weight of the neutral product was calculated weight and number of moles of the various components.

A sample calculation is shown below for the analysis of a hydrocarbon product arising from the cleavage of $Ph_3CCH_2NMe_3I$ with sodium in liquid ammonia in the presence of NH_4Cl:

Total weight of product = 0.5712 g.

Total weight of benzene solution = 2.3292 g.

Weight of 25 μl sample for vpc = 0.02307 g.

Peak ht. Ph_2CH_2 = 0.46 unit; weight Ph_2CH_2 in sample = 0.050 mg.

Peak ht. Ph_3CCH_3 = 4.54 units; weight Ph_3CCH_3 in sample = 3.65 mg.

Peak ht. Ph_2CHCH_2Ph=0.56-0.06 units; weight Ph_2CHCH_2Ph in sample = 0.88 mg.

Composition of the vpc sample therefore is:

Ph_2CH_2	0.22 weight per cent
Ph_3CCH_3	15.81 weight per cent
Ph_2CHCH_2Ph	1.25 weight per cent

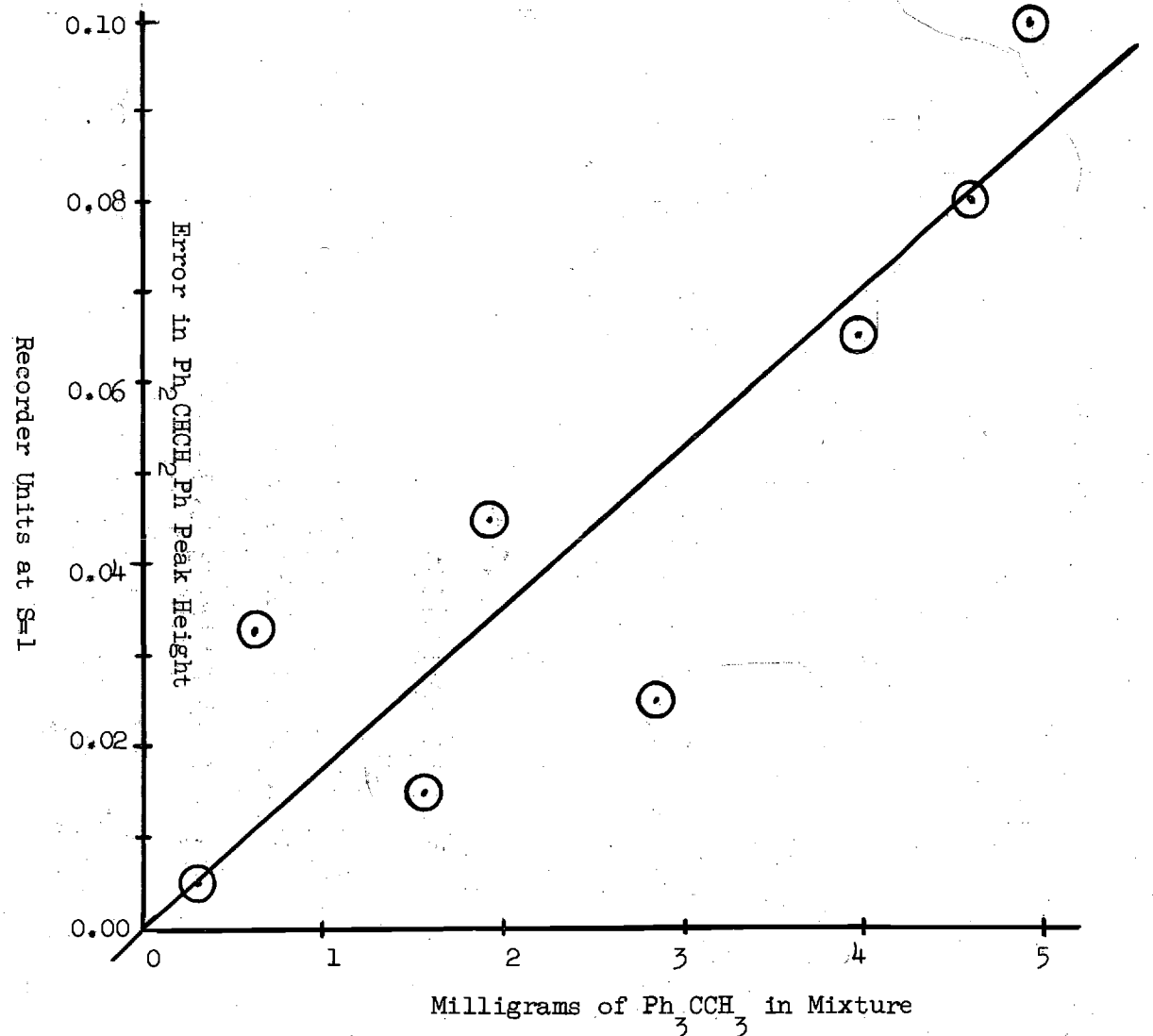


Figure 6. Correction for Ph_2CHCH_2Ph Peak Height in a Mixture of Ph_2CHCH_2Ph and a Large Excess of Ph_3CCH_3.

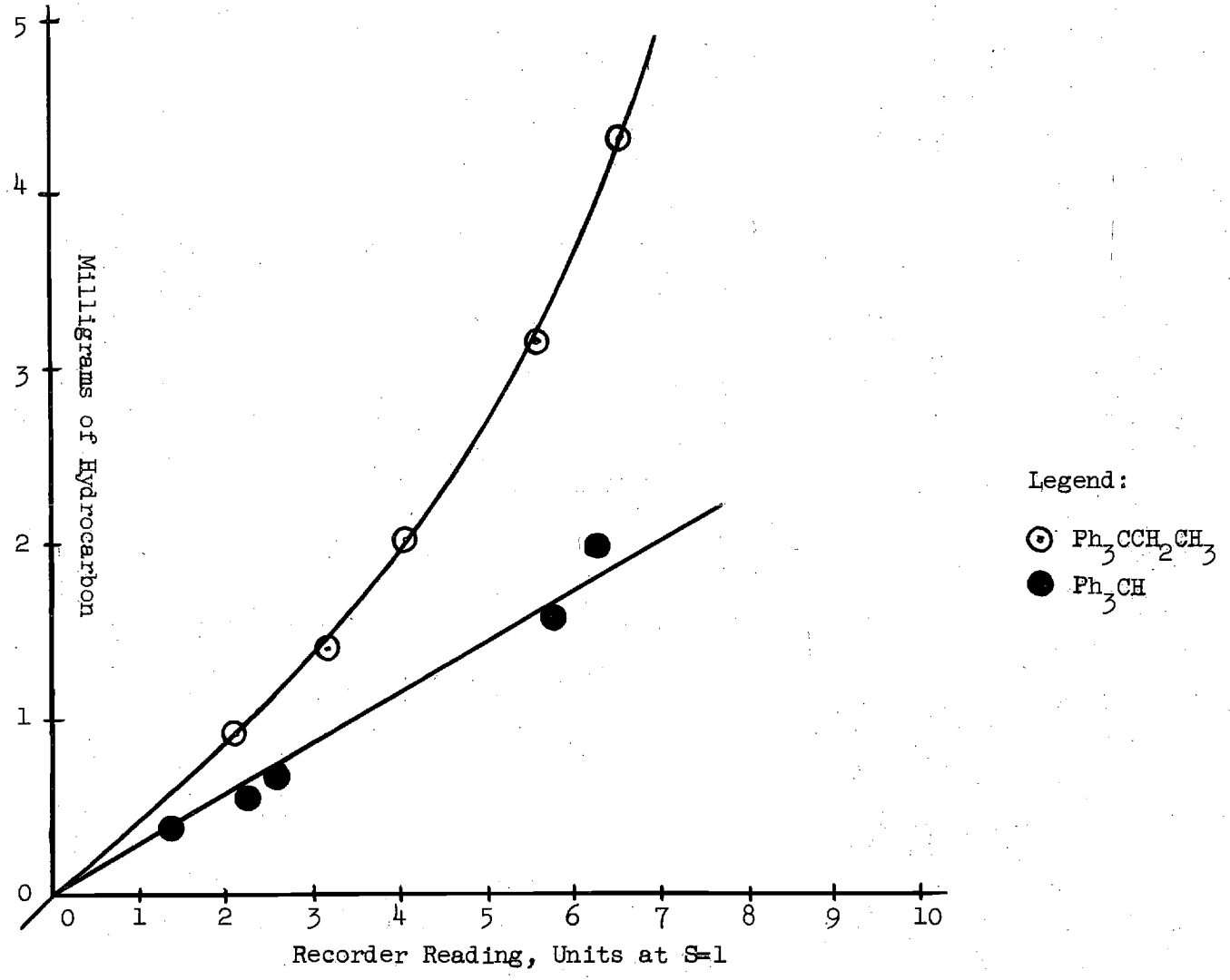


Figure 7. Calibration Curves: $Ph_3CCH_2CH_3$ and Ph_3CH

and on this basis, total amounts of hydrocarbons in the original 0.5712 gram are as follows:

Ph_2CH_2: 2.3292 g.(0.0022) = 0.0050 g. = $3.00 \pm 0.30 \times 10^{-5}$ moles

Ph_3CCH_3: 2.3292 g.(0.1581) = 0.3686 g. = $1.43 \pm 0.14 \times 10^{-3}$ moles

Ph_2CHCH_2Ph: 2.3292 g.(0.0125) = 0.0291 g. = $1.13 \pm 0.11 \times 10^{-4}$ moles

0.4024 g.

As stated earlier, the above values for yields of hydrocarbons are probably correct only within 10 per cent. Thus it is seen that roughly 30 per cent of the 0.5712 gram of product is unaccounted for. This portion may be silicone stopcock grease which was carried through the isolation procedure, or may be higher molecular weight products which did not appear on the chromatogram. In many runs, a qualitative decision as to how much of the neutral material isolated could be higher molecular weight hydrocarbons can be made by looking at the total percentage of the starting quarternary salt accounted for by products isolated.

The yields of methane, high molecular weight amine, Ph_3CCH_3, Ph_2CHCH_2Ph, and Ph_2CH_2 from this run totaled 78.1 per cent. The weight of neutral material unaccounted for as Ph_2CH_2, Ph_3CCH_3, or Ph_2CHCH_2Ph could amount to a 21.9 per cent yield of higher molecular weight hydrocarbon.

In the case of products in which triphenylethylene was present, its thermal conductivity was assumed close enough to that of the triphenylethane isomers to allow the use of the same calibration curve.

Triphenylethylene was also determined by measuring the intensity of ultraviolet absorption of a 95 per cent ethanol solution containing a

known amount of neutral product. The molar extinction coefficient ϵ of triphenylethylene used was 2.0×10^4 at 300 mμ as determined by Grovenstein.[11] The total concentration of Ph_3CCH_3 and Ph_2CHCH_2Ph in a sample of hydrocarbon could also be estimated by the method of Grovenstein[11] using ϵ as 750 at 260 mμ for both saturated hydrocarbons. Ultraviolet absorption spectra were taken with a Beckman spectrophotometer, model DK.

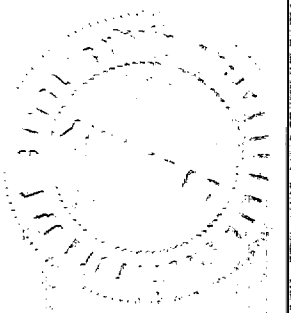
Although the determination of 1,1,1-triphenylethane and 1,1,2-triphenylethane by infrared has also been described,[11] the technique was not used in this work. The amount of 1,1,2-triphenylethane present was usually five per cent or less of the product by weight, and the mixtures analyzed were complicated by the presence of diphenylmethane and occasionally triphenylethylene.

Infrared absorption of 2,2,2-triphenylethyltrimethylammonium iodide in a KBr pellet was used to identify unreacted material from reactions with sodium or amides in liquid ammonia by comparison of the two spectra. Spectra were determined on a Perkin-Elmer double beam Model 21 infrared spectrophotometer. Pellets were made up to contain approximately two per cent by weight of compound.

Infrared spectra of other materials were taken in CS_2 solutions, at measured concentrations in 0.2 mm. or 0.5 mm. NaCl cells.

Attempts at separation and analysis of high molecular weight amines by vpc were futile, since the high temperature of the sample vaporization block on the instrument required to volatilize the amines caused a thermal decomposition of these materials. This was indicated when, using Column Q at 300° and 25 psi helium, known pure samples of $Ph_3CCH_2NMe_2$ in ether or toluene were injected. The resulting chromatogram

showed four or five peaks, yet impure samples of amine gave almost identical chromatograms. No amount of purification of $Ph_3CCH_2NMe_2$ or $Ph_3CCH_2CH_2NMe_2$ caused a decrease in the number of peaks in the chromatograms of these materials. Thermal decomposition of these amines was also indicated by heating pure $Ph_3CCH_2NMe_2$ to 300° for 15 minutes in a nitrogen atmosphere. The product after heating had a pungent, offensive odor and showed a depression in its melting point.



CHAPTER VI

DATA ON REACTIONS OF $Ph_3CCH_2NMe_3I$, Ph_3CCH_2Cl, $Ph_3CCH_2NMe_2$, Ph_3CCH_3 AND Ph_2CHCH_2Ph

Reaction of $Ph_3CCH_2NMe_3I$ with Sodium in Liquid Ammonia

A total of seven reactions of $Ph_3CCH_2NMe_3I$ with sodium in liquid ammonia were run, using the technique described in Chapter III. In the first run, an attempt was made to analyze the gaseous products by infrared absorption. However, the amount of methane produced in the reaction was too small to determine accurately. Thus, only a maximum value for the yield of CH_4 was obtained. This led to the calculation of a minimum value for the ratio of higher hydrocarbons to methane. In Tables 1 and 2, the results of these runs are summarized. The determination of CH_4 in runs 2-7 was accomplished by vpc analysis as discussed in Chapter IV. No other gaseous hydrocarbons were found as products. The nonvolatile hydrocarbon products were also determined quantitatively by vpc after isolation from the residue in the reaction vessel, as outlined in Chapter III. The average yield of methane from runs 2-7 is 0.0262 per cent with an average deviation of ±0.0030 per cent which amounts to 11.5 per cent of the average yield. A deviation of this size corresponds approximately to the reproducibility of the peak heights of methane vpc curves at CH_4 pressures of less than one millimeter.

The average yield of hydrocarbon (Ph_2CH_2, Ph_2CHCH_2Ph and Ph_3CCH_3) from runs 1-4 and 6-7 amounts to 82.7 ± 11.0 per cent. The average

Table 1. Products of the Reaction of $Ph_3CCH_2NMe_3I$ with Sodium in 200 ml. of Liquid NH_3 at -33°.

Run No.	Initial Salt mmoles	Salt Consumed mmoles	Sodium mmoles	Yields of Products, mmoles and per cent[a]				
				CH_4 mmoles x 10^{+4}	Ph_2CH_2 mmoles	Ph_2CHCH_2Ph mmoles	Ph_3CCH_3 mmoles	Amine[b] mmoles
1	2.82	2.82	5.65	(<107[c]) (<0.38%)[c]	(0.0108[d]) (0.38%)[d]	0.197 6.99%	2.39 84.86%	0.150 5.31%
2	2.01	1.96	4.35	5.45 0.0278%	0.0661 3.37%	0.0817 4.17%	1.32 67.35%	"Trace"[e]
3	2.03	2.03	4.78	5.35 0.0264%	0.0937 4.62%	0.0996 4.91%	1.62 79.80%	"Trace"[e]
4	2.03	2.03	4.78	5.58 0.0275%	0.121 5.96%	0.115 5.67%	1.78 87.68%	"Trace"[e]
5	2.10	2.03	4.78	4.10 0.0202%	0.0710 3.50%	0.183 9.03%	2.34 115%	0.159 7.82%
6	2.26	2.19	4.56	5.08 0.0232%	0.0284 1.30%	0.101 4.60%	1.32 60.41%	0.285 13.01%
7	1.69	1.65	3.48	5.30 0.0321%	0.0238[f] 1.44%[f]	0.0986[f] 5.98%[f]	1.10[f] 66.41%[f]	0.116 7.00%

[a]Yields are based on the number of mmoles of quaternary salt consumed.

[b]Molecular weight of the amine assumed to be 315.

[c]Estimated by infrared absorption.

[d]The hydrocarbon product from this run was vacuum sublimed before analysis. A portion of the lower boiling Ph_2CH_2 therefore could have been lost.

[e]Not determined quantitatively.

[f]A small amount of hydrocarbon product was lost in the isolation procedure.

Table 2. Ratios of RH/CH_4 and Extent of Rearrangement of RH in the Reaction of $Ph_3CCH_2NMe_3I$ with Na in Liquid NH_3 at -33°.

Run No.	Moles $CH_4 \times 10^{+7}$	Total[a] Moles RH $\times 10^{+3}$	Ratio RH/CH_4	Corrected[b] Ratio $3\ RH/CH_4$	Percentage Rearrangement[c]
1	(<107)	2.598±0.260	(>243)	(>729)	(>8.0)
2	5.45±0.42	1.468±0.147	2700±480	8100±1400	10.0
3	5.35±0.41	1.814±0.181	3400±600	10200±1800	10.7
4	5.58±0.52	2.016±0.202	3610±700	10800±2100	11.7
5	4.10±0.30	(<2.590)	(<6300)	(<18900)	9.8
6	5.08±0.36	1.452±0.145	2860±490	8600±1500	8.9
7	5.30±0.38	1.218±0.122	2300±390	6900±1200	10.0

Average Corrected Ratio RH/CH_4, runs 2,3,4,6,7 = 8900±1600.

Average Extent of Rearrangement of RH, runs 2-7 = 10.2±0.7%.

[a] Total moles of hydrocarbons (RH) = moles Ph_2CH_2 + moles Ph_2CHCH_2Ph + moles Ph_3CCH_3.

[b] The ratio of RH/CH_4 was corrected for an equal number of R- and CH_3- groups on the salt $R_nN(CH_3)_{4-n}X$ according to the formula

$$\text{Corrected Ratio} = \left[(4-n)/n\right](RH/CH_4).$$

[c] $$\text{Percentage Rearrangement} = \left[(\text{moles } Ph_2CH_2 + Ph_3CHCH_2Ph)/RH\right] 100.$$

deviation is 13.3 per cent of the average yield. This deviation is somewhat greater than the variation in peak heights observed on the chromatographs used in the hydrocarbon analyses. The remainder of the deviation probably can be attributed to loss of hydrocarbon in the isolation procedure. However, the yield of hydrocarbon from run 5 is considerably in excess of 100 per cent. This yield cannot be accounted for except for the possibility of an error in the determination itself.

When the percentage yields of the products from runs 1-4 and 6-7 are summed, the average total of products found is 87.0 ± 8.6 per cent. The remaining 13 per cent unaccounted for might be attributed to higher molecular weight products which were not observed on vpc chromatograms, products which were extracted into the water phase in the isolation procedure, or error in estimation of the quaternary salt consumed.

According to the reaction

$$Ph_3CCH_2NMe_3I + 2\ Na \xrightarrow{NH_3} Ph_3CCH_2NMe_2 + CH_4 + NaI + NaNH_2,$$

the yield of amine from runs 1-7 in Table 1 should amount to an average of 0.0262 per cent. However, as seen from Table 1, roughly 400 times this amount of an amine was recovered. The amine product melted at 86-88°, showed a mixed melting point depression with $Ph_3CCH_2NMe_2$, and exhibited different infrared and nuclear magnetic resonance spectra when compared with the spectra of $Ph_3CCH_2NMe_2$. The origin and structure of this amine will be discussed in the last section of this chapter and in Chapter VI.

In all the reactions of $Ph_3CCH_2NMe_3I$, Ph_3CCH_2Cl and Ph_2CHCH_2Ph with sodium in liquid ammonia, a red color developed immediately after

addition of the sodium. When excess sodium was used, the resulting dark blue color soon masked the red, except for the region of the reaction vessel immediately above the surface of the solvent where NH_3 was evaporating. Judging qualitatively from the rate of gas evolution, the reaction of $Ph_3CCH_2NMe_3I$ with Na is extremely fast, apparently being limited only by the rate of sodium dissolution.

The presence of Ph_2CHCH_2Ph and Ph_2CH_2 in the reaction products is believed to result from the rearrangement

$$Ph_3CCH_2:^- \longrightarrow Ph_2\overset{\cdot\cdot}{C}CH_2Ph^-$$

followed by protonation of the rearranged carbanion. The rearranged hydrocarbon was then partially cleaved by sodium in liquid ammonia to yield Ph_2CH_2 and $PhCH_3$. These reactions were demonstrated by several experiments.

Reaction of Ph_3CCH_2Cl with Sodium in Liquid Ammonia

For this experiment, 3.41 mmoles of Ph_3CCH_2Cl were dissolved in 250 ml. of liquid ammonia and 6.95 mmoles of sodium metal were added. The reaction was run using the same technique as used for quaternary ammonium salts, and the technique of isolation of higher molecular weight products was also similar. A dark red color developed in the ammonia solution which lasted the three hours duration of the run. Analysis of products by vpc indicated a 56.55 per cent yield of Ph_3CCH_3, 4.64 per cent of Ph_2CHCH_2Ph, 1.22 per cent Ph_2CH_2 and 18.80 per cent of $Ph_2C{=}CHPh$. It is interesting to note that a 9.39 per cent yield of rearranged saturated hydrocarbon resulted, similar to the amount found in products from

$Ph_3CCH_2NMe_3I$ + Na in liquid NH_3. The presence of $PhCH_3$ was also shown by vpc, but the amount was not determined quantitatively. It is suspected that the triphenylethylene in this reaction results from an α-elimination, with either $NaNH_2$ or an organosodium product acting as the strong base required:

$$Ph_3CCH_2Cl \xrightarrow{B:} Ph_3\overset{\cdot\cdot}{\underset{-}{C}}CHCl \longrightarrow Ph_2C{=}CHPh + Cl^-$$

This reaction has been shown by Zimmerman and Swentowski[12] to occur between Ph_3CCH_2Cl and amylsodium in ether-isooctane at 35°. However, these authors were unable to effect any reaction between $NaNH_2$ and Ph_3CCH_2Cl in refluxing ether for 30 minutes. The products of rearrangement, Ph_2CHCH_2Ph, Ph_2CH_2 and $PhCH_3$, were not reported by Charlton, Dostrovsky, and Hughes[14] in the reaction of Ph_3CCH_2Cl with sodium in liquid ammonia followed by treatment of the mixture with NH_4Cl.

Reactions of Ph_3CCH_3 and Ph_2CHCH_2Ph with Sodium in Liquid Ammonia

Experiments involving the reaction of various hydrocarbon products with sodium in liquid ammonia under the usual reaction conditions were performed. Solutions of Ph_3CCH_3 and of Ph_2CHCH_2Ph in liquid ammonia were treated with sodium and sodium amide with the results shown in Table 3.

Thus it is shown that the Ph_2CH_2 found as a product of the cleavage of $Ph_3CCH_2NMe_3I$ with sodium in liquid ammonia can result from the cleavage of the hydrocarbon Ph_2CHCH_2Ph with sodium. The reaction is presumed to be

Table 3. Products of Reactions of Hydrocarbons with Sodium and Sodium Amide in 200 ml. of Liquid Ammonia at -33°.

Reaction	Hydrocarbon Used mmoles	Na or $NaNH_2$ Used mmoles	Isolated Products Found
Ph_3CCH_3 + Na	1.49	3.26	Ph_3CCH_3 (only this by vpc)
Ph_3CCH_3 + $NaNH_2$	1.39	3.69	Ph_3CCH_3 (only this by vpc)
Ph_2CHCH_2Ph + Na	1.55	3.04	Ph_2CH_2, $PhCH_3$, Ph_2CHCH_2Ph and small amounts of unidentified products.*

*Using vpc column Q at 300°, 25 psi, 65 cc./min. helium, $PhCH_3$ had a retention time of 0.6 minute and Ph_2CH_2 4.0 minutes. The retention time of Ph_2CHCH_2Ph at these conditions is ca. 30 minutes. The unknowns, comprising less than 10 per cent of the total peak areas, showed retention times of 1.1, 5.5, and 7.4 minutes. Ph_2CH_2 was apparently cleaved in good yield; the molar ratio of Ph_2CH_2/Ph_2CHCH_2Ph found by vpc was 3.11/1.39 = 2.24.

$$Ph_2CHCH_2Ph + 2\ Na \longrightarrow Ph_2C^-\ Na^+ + PhCH_2^-\ Na^+$$

although no attempt was made to determine the stoichiometry of the reaction.

Reaction of $Ph_3CCH_2NMe_2$ with Sodium in Liquid Ammonia

It was shown that $Ph_3CCH_2NMe_2$ is not cleaved by sodium in liquid ammonia to a significant extent. In this experiment, 0.665 mole of $Ph_3CCH_2NMe_2$ in 100 ml. of liquid ammonia was treated with 1.74 mmoles of sodium. After 2-1/2 hours, 85 per cent of the amine was recovered

unreacted as shown by a mixed m.p. with authentic $Ph_3CCH_2NMe_2$. VPC analysis of the small amount of neutral product showed only one very small peak with a retention time corresponding to that of Ph_3CH. The yield of Ph_3CH was estimated at 0.7 per cent. When the reaction was repeated in the presence of 5.60 mmoles of NH_4Cl, no neutral products with vpc retention time up to 45 minutes were obtained, and an approximately 85 per cent yield of unchanged amine was recovered.

Reaction of $Ph_3CCH_2NMe_3I$ with Sodium in Liquid Ammonia in the Presence of Ammonium Chloride

Five runs were made, using the technique described in Chapter III. The NH_4Cl used was transferred from one of the retorts into the liquid ammonia at the same time as the quaternary salt. The sodium metal was added five to fifteen minutes later, after stirring the solution thoroughly. Results of the runs were complicated by the fact that the reaction of sodium with ammonium chloride to evolve hydrogen was found to be faster than that between sodium and $Ph_3CCH_2NMe_3I$. Thus, the yields of the higher molecular weight hydrocarbon products isolated were less than in runs where no NH_4Cl was used. Also, the relatively large amount of hydrogen evolved diluted the CH_4 in product gases making analysis more prone to variation and error. Results of the five runs are included in Tables 4 and 5. In run 4, an abnormally high yield of methane was found. The reason for this high yield is unknown.

No red color was observed during the reactions of $Ph_3CCH_2NMe_3I$ with sodium in the presence of NH_4Cl; the absence of color indicates a rapid protonation of any colored carbanions formed. Also significant is

Table 4. Products of the Reaction of $Ph_3CCH_2NMe_3I$ with Na and NH_4Cl in 200 ml. of Liquid Ammonia at -33°.

Run No.	Initial Salt mmoles	Salt Consumed mmoles	Sodium mmoles	NH_4Cl mmoles	Yields of Products, Millimoles and Per Cent[a]				
					CH_4 mmoles x 10^{+4}	Ph_2CH_2 mmoles	Ph_2CHCH_2Ph mmoles	Ph_3CCH_3 mmoles	Amine mmoles
1	2.39	1.69	6.95	10.3	(<48.5)[b] (<0.287%)[b]	0[c]	0.0636[c] 3.76%	1.291[c] 76.41%	"Trace"[d]
2	2.28	1.56	7.82	7.85	9.00 0.0576%	0[c]	0.0774[c] 4.96%	1.282[c] 82.15%	"Trace"[d]
3	2.50	(<2.50)[e]	6.30	6.55	(>0.380)[e] (>0.00138)[e]	0.0178 0.71%	0.129 5.16%	1.78 71.20%	"Trace"[d]
4	2.26	1.82	7.83	8.41	24.8 0.136%	0.0250 1.37%	0.0929 5.10%	1.243 68.31%	"Trace"[d]
5	2.26	2.01	8.26	8.41	3.87 0.0192%	0.0300 1.49%	0.1128 5.61%	1.427 71.00%	"Trace"[d]

[a] Yields are based on mmoles of quaternary salt consumed in all except run 3, where it is based on mmoles of initial salt.

[b] Methane was estimated by infrared absorption.

[c] Vapor phase chromatographic analysis of this sample was made several months after the sample was isolated, and after a vacuum sublimation had been done.

[d] The designation "Trace" here means too small an amount to recover and weigh, i.e., less than 1 per cent.

[e] During the reaction the liquid ammonia solution boiled out of the vessel and one of the mercury valves failed. An indefinite amount of quaternary salt and NH_4CL was lost, as well as some methane and hydrogen.

Table 5. Ratios of RH/CH_4 and Extent of Rearrangement of RH in the Reaction of $Ph_3CCH_2NMe_3I$ with Na and NH_4Cl in Liquid Ammonia at -33°.

Run No.	Moles $CH_4 \times 10^{+7}$	Total[a] Moles RH $\times 10^{+3}$	Ratio RH/CH_4	Corrected Ratio 3 RH/CH_4	Percentage Rearrangement[c]
1	(<48.5)	1.354±0.135	(>279)	(>837)	≥ 4.7
2	9.00±1.06	1.359±0.136	1490±330	4480±980	≥ 5.7
3	(>0.344)	1.927±0.193	(<56000)	(<168000)	7.6
4	(24.8±1.5)[b]	1.361±0.136	(54.8±8.8)[b]	(164±26)[b]	8.7
5	3.87±1.23	1.570±0.157	4060±650	12200±2000	9.1

Average extent of rearrangement, runs 3-5 = 8.5±0.6%

[a] Total moles hydrocarbon (RH) = moles Ph_2CH_2 + moles Ph_2CHCH_2Ph + moles Ph_3CCH_3.

[b] See discussion in text.

[c] Percentage rearrangement = $\left[(\text{moles } Ph_2CH_2 + Ph_2CHCH_2Ph)/RH\right]100$.

the fact that only very small amounts of amine were produced, as opposed to the abnormally high yields of amine in reactions in which NH_4Cl was not present.

Reaction of $Ph_3CCH_2NMe_3I$ with Sodium in Dioxane at 99°

One reaction was run, using the apparatus depicted and described by Blanchard.[42] The apparatus consisted of a Morton high-speed stirring assembly and a system of mercury valves and bubblers so as to permit blanketing or sweeping the system with dry nitrogen, and collection of gaseous reaction products over saturated brine after washing them in a standard solution of HCl to remove volatile amines. It is important to recall that Stevenson[6] noted that quantitative recovery of gaseous products was not possible except in a very fast run (ca. 15 minutes) with this apparatus, due to leakage about the stirrer shaft.

A mixture of 1.48 grams (64.3 mmoles) of sodium metal and 500 ml. of purified dioxane were heated to reflux in a one-liter Morton flask. After the sodium had become molten, the mixture was stirred at high speed for 30 minutes to insure that the dioxane and the nitrogen atmosphere were dry. Ten grams (22.6 mmoles) of $Ph_3CCH_2NMe_3I$ was added in six portions over a 30 minute period to the rapidly stirred mixture of sodium and dioxane. A light brown color developed in the mixture. After the addition of quaternary salt was completed, the mixture was stirred for an additional 30 minutes. Gaseous reaction products were swept through two gas scrubbers containing 900 ml. of 0.1022 N HCl and into a ten-liter

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42. Blanchard, op. cit., pp. 36-38, 40.

inverted bottle filled with saturated brine. A total of 3.50 liters of gaseous product diluted with nitrogen was collected. Analysis of this gas by vpc indicated a yield of 0.664 mmole or 2.94 per cent methane, based on initial quaternary salt taken.

Following the 30 minutes of stirring after addition of the quaternary salt, 200 ml. of dioxane was distilled from the reaction mixture. This solvent was combined with the 900 ml. of standard HCl from the scrubbers described above. Titration of this dioxane-aqueous HCl mixture with 0.09938 N NaOH indicated a yield of 2.20 mmoles or 9.73 per cent of volatile amine, assumed to be $(CH_3)_3N$.

The reaction mixture in dioxane was forced by nitrogen pressure onto a large excess of Dry Ice (ca. 500 grams) to carbonate any carbanions present. After standing overnight, the carbonated mixture was treated with 95 per cent ethanol to destroy any sodium remaining. The mixture was evaporated to dryness on a Rotovac at steam bath temperature, then extracted with an ether-water mixture. The two phases were separated and filtered. Only 0.12 gram of a black, inorganic residue (probably graphite stirrer packing material) was recovered. Acidification of the basic aqueous phase failed to produce a precipitate, showing that no appreciable amount of carbanions was present in the dioxane reaction mixture at the end of the run in the Morton apparatus.

The ether phase was dried over KOH pellets and saturated with dry HCl gas to precipitate any amine product. The amine hydrochloride from this procedure was filtered off, washed with ether, then dissolved in water. The aqueous solution was made basic, precipitating the amine. After filtration, 3.92 grams of a semisolid amine was obtained.

Recrystallization of this product from 95 per cent ethanol gave a 2.79 gram yield of tan crystals which melted sharply at 111.9-112.0°. A mixture of this amine and authentic $Ph_3CCH_2NMe_2$ (m.p. 109.4-111.2°) melted at 108.5-110.5°. Comparison of infrared spectra of the two amines in CS_2 showed identical absorption frequencies, with minor differences in intensities. The amine product was thus shown to be $Ph_3CCH_2NMe_2$. The 3.92 grams of crude product isolated corresponds to a 57.60 per cent yield based on the initial quaternary salt taken.

The ether phase from which the $Ph_3CCH_2NMe_2$ was extracted was next washed with aqueous NaOH and water. After drying the solution with anhydrous $MgSO_4$, the ether solvent was removed on a Rotovac. This procedure yielded 2.26 grams of viscous brown neutral material. The neutral product was dissolved in benzene and analyzed by vpc. Since the weight of benzene used was not accurately determined, it was necessary to assume that all the brown oil was hydrocarbon. The weight percentage of components observed by vpc was then used to calculate the yields of the various hydrocarbons from the weight of oil isolated. Yields of hydrocarbons found (based on the initial quaternary salt) are as follows:

Ph_2CH	Not Found
Ph_2CHCH_2Ph	1.092 mmoles or 4.84 per cent
Ph_3CCH_3	4.975 mmoles or 22.02 per cent
$Ph_2C{=}CHPh$	2.70 mmoles or 11.95 per cent.

The presence of triphenylethylene indicated that an elimination involving the quaternary salt and an organosodium base was occurring simultaneously with the cleavage of $Ph_3CCH_2NMe_3I$ with sodium. Accordingly, the $Ph_2C{=}CHPh$

was not counted as a cleavage product. From the cleavage, a total of 6.067 mmoles of Ph_3CCH_3 and Ph_2CHCH_2Ph were obtained.

The ratio of hydrocarbons to methane is $6.067 \times 10^{-3} / 0.664 \times 10^{-3} = 9.15$, and corrections for statistically equal numbers of groups on nitrogen, the ratio becomes 27.5. This is probably a maximum value, since Stevenson[6] noted that quantitative recovery of methane from the Morton apparatus was only achieved in runs of very short duration. Perhaps a more realistic value of the ratio could be obtained by the ratio of trimethylamine to methane, since they should be of approximately the same volatility at 99° and should be lost in roughly the same ratio as their relative amounts in the product gases. Also, the trimethylamine found may be compared with the yield of $Ph_2C{=}CHPh$ from the presumed α - elimination side reaction. The ratio of NMe_3/CH_4 found is 3.32, or when statistically corrected, approximately 10. However, if one mole of Me_3N is produced for every mole of $Ph_2C{=}CHPh$, then much of the Me_3N found could have come from the side reaction.

While no red color was observed in the dioxane solution during the reaction, it is interesting that the Ph_2CHCH_2Ph arising from a colored carbanion was found, and amounted to 18 per cent of the hydrocarbons from cleavage.

Reaction of $Ph_3CCH_2NMe_3I$ with Sodium Amide and Potassium Amide in Liquid Ammonia at -33°

The presence of unexpected, large amounts of an amine (which was not $Ph_3CCH_2NMe_2$) in the reaction products of $Ph_3CCH_2NMe_3I$ with Na in NH_3, and the fact that this amine is not found when NH_4Cl is present in the

reaction mixture, indicated that a side reaction between $NaNH_2$ and $Ph_3CCH_2NMe_3I$ was occurring. This was shown by a series of experiments in which $Ph_3CCH_2NMe_3I$ was reacted with $NaNH_2$ or KNH_2 in liquid NH_3. The results of these runs are summarized in Table 6. Melting points of the crude amine products as first isolated from runs 1-4 were as follows:

Run 1: m.p. 85-90°

Run 2: m.p. 85.0-87.5°

Run 3: m.p. 84.5-86.0°

Run 4: m.p. 86-88°.

After one vacuum sublimation at 75-110° and 10μ, the product from Run 1 melted at 86-88°. Three vacuum sublimations of the product from Run 2 gave a product which melted at 86.0-87.0°. From these data, it is apparent that the amine as first isolated is relatively pure; probably 95 per cent or greater purity. The amine product from these runs proved to be identical with that isolated from reactions of $Ph_3CCH_2NMe_3I$ with Na in liquid NH_3, as judged by mixed melting points and infrared spectra. Triphenylethylene, a product not found in the reactions of sodium with the quaternary salt in liquid ammonia, was isolated in small amounts in two of the runs.

The use of KNH_2 gave rise to much higher yields of amine. This probably is due largely to the much higher solubility of KNH_2 in liquid ammonia as compared with $NaNH_2$. Although no quantitative data on the solubility of $NaNH_2$ in NH_3 at -33° were available from the literature,

Table 6. Products of the Reaction of $Ph_3CCH_2NMe_3I$ with $NaNH_2$ or KNH_2 in Liquid NH_3 at -33°.

Run No.	Initial Salt mmoles	Salt Consumed mmoles	Base Used	Initial Base mmoles	Yields of Products, Millimoles and Per Cent					
					$CH_4 \times 10^{+4}$ mmoles	Ph_2CH_2 mmoles	Ph_2CHCH_2Ph mmoles	Ph_3CCH_3 mmoles	$Ph_2C{=}CHPh$ mmoles	Amine[a] mmoles
1[d]	2.50	0.90	$NaNH_2$	5.75	0[b]	--Total[c] ≤ 0.317 (35.46%)--			0.0057[c] 0.64%	0.267 29.87%
2[e]	4.63	2.84	$NaNH_2$	10.00	(64.7) (0.23%)	--Total[c] ≤ 0.39 (13.71%)---			Not Determined	1.82 63.9%
3[f]	4.64	4.64	KNH_2	12.0	10.3 0.0222%	0.0076 0.16%	0.149 3.21%	0.0710 1.53%	0.108 2.33%	4.32 93.1%
4[g]	31.2	25.8	KNH_2	70.3	----------Not Determined----------					25.1 97.4%

[a] Assume molecular weight of 315 for the amine.

[b] Analysis attempted by infrared absorption.

[c] Analyses accomplished by ultraviolet absorption; yield given is the total for all 3 hydrocarbons.

[d] Run in 200 ml. liquid NH_3; Reaction time 2 hours.

[e] Run in 200 ml. liquid NH_3; Reaction time 12 hours.

[f] Run in 200 ml. liquid NH_3; Reaction time 20 hours.

[g] Run in 600 ml. liquid NH_3; Reaction time 18 hours.

Franklin[43] reports that KNH_2 is soluble in liquid ammonia at -33.5° to the extent of 45 grams KNH_2 per 100 ml. liquid ammonia while $NaNH_2$ has a "much lower" solubility at the same temperature. Extrapolation of solubility data for $NaNH_2$ at higher temperature[44] in liquid ammonia indicates the solubility may be of the order of 0.09 grams $NaNH_2$ per 100 grams liquid ammonia at -33°.

In all the reactions of $NaNH_2$ or KNH_2 with $Ph_3CCH_2NMe_3I$ listed in Table 6, a red or reddish-brown color developed in the solution. This is explained in run 3 by the presence of both $Ph_2C{=}CHPh$ and Ph_2CHCH_2Ph which give highly colored intermediates with strong bases in liquid ammonia.

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43. E. C. Franklin, Z. phys. Chem., 69, 290 (1909).

44. S. Sigetomi, J. Soc. Chem. Ind. Japan, Suppl. binding, 41, 409-410 (1938).

CHAPTER VII

REACTIONS OF 3,3,3-TRIPHENYLPROPYLTRIMETHYLAMMONIUM IODIDE

Methiodide of the Unknown Amine from $Ph_3CCH_2NMe_3I$ and $NaNH_2$

In the initial preparation of this salt, 0.223 gram (0.708 mmole, assuming MW = 315) of amine (m.p. 86-88°) obtained from the reaction of $NaNH_2$ with $Ph_3CCH_2NMe_3I$ (called run 2 in Table 6 of Chapter IV) was combined with 0.10 ml. (1.61 mmoles) of CH_3I in 25 ml. of dry acetone. After eight days, 0.130 gram of white crystals were recovered from the mixture. After drying in vacuo at 56° for 3 hours, the product melted at 269-271° with decomposition. One recrystallization of the methiodide from 95 per cent ethanol followed by a recrystallization from acetone yielded white crystals which melted sharply at 271° with decomposition. Infrared spectra of the unknown methiodide and known $Ph_3CCH_2NMe_3I$ run in KBr pellets showed marked differences. A sample of methiodide prepared from the amine product of $Ph_3CCH_2NMe_3I$ and KNH_2 (run 3, Table 6, Chapter IV) melted at 270-271° and a mixture of the two samples of unknown methiodide showed no melting point depression.

Anal. Found:* I, 26.32, 26.55. Calculated for $C_{24}H_{28}NI$: I, 27.75. Additional unknown methiodide for use in reactions with Na in liquid NH_3 was prepared from the amine product of KNH_2 and $Ph_3CCH_2NMe_3I$ (run 4 in Chapter IV) in approximately 58 per cent yield. The unknown quaternary

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*The analyst reported a trace of ash in this sample.

salt thus prepared melted at 265-269.5° with decomposition.

Reactions with Sodium in Liquid Ammonia

Three runs were made, employing the same technique as described in Chapter III. Results of these runs are summarized in Table 7. Due to the inaccurate method of determination of Ph_3CH and $Ph_3CCH_2CH_3$ in run 1, the ratio RH/CH_4 is only an approximation.

Reactions with Sodium and Ammonium Chloride in Liquid Ammonia

Two runs were made by the usual technique. However, the reaction of NH_4Cl with sodium proved to be much faster than the cleavage reaction and very little quaternary salt was consumed in either run. Also, the methane and ethylene produced were diluted by hydrogen to such a low concentration that accurate determination was very difficult. The only useful data to be gained from the runs was that apparently the ratio of $Ph_3CCH_2CH_3$ to Ph_3CH is not altered greatly upon the addition of NH_4Cl to a reaction mixture of the quaternary salt and sodium.

Structure of the Unknown Amine and Methiodide

The production of Ph_3CH, $CH_2=CH_2$ and $Ph_3CCH_2CH_3$ from reaction of the unknown quaternary salt with sodium was shown by the comparison of vpc retention times. In the case of ethylene, such gases as methane, ethane, and butane were ruled out on the basis of having widely differing retention times from C_2H_4. Using column "J" at 32° and 5 psi, the following retention times were observed: Air, 1.8 minutes; methane, 3.0 minutes; ethane, 12.1 minutes; ethylene, 30 minutes; butane, 61 minutes. The retention time of a known sample of Ph_3CH was exactly the same as for the peak of one of the nonvolatile products of the unknown quaternary salt

Table 7. Products of the Reaction of the "Unknown" Methiodide ($Ph_3CCH_2CH_2NMe_3I$) with Sodium in 200 ml. of Liquid Ammonia at -33°, and Ratios of RH/CH_4

Run No.	Initial Salt mmoles	Salt Consumed mmoles	Sodium mmoles	Yields of Products, mmoles and per cent					Ratio[b] RH/CH_4	Corrected Ratio $3\ RH/CH_4$
				CH_4	C_2H_4	Ph_3CH	$Ph_3CCH_2CH_3$	Amine[a]		
1	1.64	1.64	4.78	0.0659 4.01%	Not Determined	~0.473[c] ~28.8%	~0.750[c] ~45.7%	0.0305 1.86%	~18.6	~55.8
2	2.51	2.51	6.96	0.0606 2.42%	0.3745 14.9%	0.302 12.0%	1.694 67.5%	0.0365 1.45%	32.9	98.7
3	1.11	1.11	2.61	0.0347 3.13%	0.1298 11.7%	0.169 15.23%	0.806 72.6%	Not Determined	28.1	84.3

Average Corrected Ratio $3RH/CH_4$, runs 2-3 = 92±16

[a]Molecular weight of the amine is assumed to be 315.

[b]Hydrocarbon (RH) = moles Ph_3CH + moles $Ph_3CCH_2CH_3$.

[c]Estimated by vpc analysis using the calibration curve made up for Ph_3CCH_3.

Table 8. Products of the Reaction of the "Unknown" Methiodide ($Ph_3CCH_2CH_2NMe_3I$) with Sodium and Ammonium Chloride in 200 ml. of Liquid Ammonia at -33°, and Ratios of RH/CH_4

Run No.	Initial Salt mmoles	Salt Consumed mmoles	Sodium mmoles	NH_4Cl mmoles	Yields of Products, mmoles and per cent					Ratio RH/CH_4	Corrected Ratio $3\ RH/CH_4$
					CH_4	C_2H_4	Ph_3CH	$Ph_3CCH_2CH_3$	Amine		
1	2.74	1.03	11.7	12.5	0.00194 0.189%	Not Determined	*	*	0.0194 1.88%	----	---
2	2.18	0.34	9.1	9.9	(0.00024) (0.0705%)	(0.000503) (0.148%)	0.0439 12.9%	0.201 59.0%	"Trace"	(1020)	(3060)

*Found by vpc but not determined quantitatively. Peak areas were roughly in the ratio 3 $Ph_3CCH_2CH_2$: 1 Ph_3CH. Total weight of neutral product isolated from this run was 0.037 gram.

cleavage on two different vpc columns, "Q" and "O." Retention times: 4.2 minutes on column "O," 20.9 minutes on column "Q." A portion of the non-volatile product from run 1 of unknown methiodide and sodium was injected into a preparative scale vpc type "O" column two meters in length and the two constituents were separated and isolated. The material with retention time corresponding to Ph_3CH was mixed with an authentic sample of triphenylmethane and reinjected into a vpc column "O." No separation of peaks resulted. The second constituent of the product had a retention time which coincided with $Ph_3CCH_2CH_3$ and $Ph_2C{=}CHPh$ on column "Q" (32 minutes). To further rule out $Ph_2C{=}CHPh$ as a possibility, the ultraviolet spectra of the unknown hydrocarbon and triphenylethylene at similar concentrations in 95 per cent ethanol were compared. The authentic $Ph_2C{=}CHPh$ showed a strong maximum at 300 mμ, while the unknown showed no such maximum. Calculations indicated a maximum of 3 weight per cent $Ph_2C{=}CHPh$ could be present in the unknown. The infrared spectrum of the hydrocarbon product from the unknown methiodide and sodium (run 2, Table 7) which vpc indicated as having a composition of roughly 14 per cent Ph_3CH and 86 per cent $Ph_3CCH_2CH_3$ was run in CS_2. Then a synthetic sample containing 16.5 per cent Ph_3CH and 83.5 per cent $Ph_3CCH_2CH_3$ was run in CS_2. Then a synthetic sample containing 16.5 per cent Ph_3CH and 83.5 per cent $Ph_3CCH_2CH_3$ was prepared and its spectrum taken in CS_2 at a similar concentration. The spectra were very similar, showing identical absorption wavelengths and differing only slightly in intensity. One unexplained, spurious peak of medium intensity appeared at 14.81 microns on the spectrum of the unknown hydrocarbon mixture which was not present in the spectrum of the synthetic sample.

The presence of $Ph_3CCH_2CH_3$ as a reaction product led immediately to the possibility that the structure of the quaternary salt was either

$Ph_3C\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}NMe_3I$ (Structure A) or $Ph_3CCH_2CH_2NMe_3I$ (Structure B).

The presence of Ph_3CH and $CH_2{=}CH_2$ as products might then be explained as coming from an elimination

$$Ph_3CCH_2CH_2{:}^- \longrightarrow Ph_3C{:}^- + CH_2{=}CH_2$$

of the type reported by Wooster and Morse[45] in the reaction of $Ph_3CCH_2CH_2I$ with sodium in liquid ammonia, followed by treatment with NH_4NO_3.

Structure of the unknown amine was shown to be $Ph_3CCH_2CH_2NMe_2$ by comparison of physical properties with a known sample of the amine, prepared by the method outlined in Chapter II. A mixture of unknown amine and $Ph_3CCH_2CH_2NMe_2$ showed no melting point depression. Infrared spectra of the two amines in CS_2 were identical, and different from that of a known sample of $Ph_3CCH_2NMe_2$. The combination of chemical evidence from reactions of the quaternary salt and well-defined structure proof fot its tertiary amine precussor leaves no doubt that the structure of the unknown methiodide is $Ph_3CCH_2CH_2NMe_3I$, a compound not reported in the literature.

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45. C. B. Wooster and R. A. Morse, J. Am. Chem. Soc., 56, 1735 (1934). See also H. Pines and L. Schaap, J. Am. Chem. Soc., 80, 4378-4381 (1958).

CHAPTER VIII

REACTIONS OF 2,2-DIMETHYLPROPYLTRIMETHYLAMMONIUM IODIDE

Three reactions of $Me_3CCH_2NMe_3I$ with sodium in liquid ammonia were run using the same technique for this quaternary salt as was used for the runs involving $Ph_3CCH_2NMe_3I$ and $Ph_3CCH_2CH_2NMe_3I$. Results of these runs are included in Table 9. A blue solution was observed in runs 2 and 3 indicating the presence of excess sodium over the theoretical amount required to react with the $Me_3CCH_2NMe_3I$. In run 1, a cloudy white solution was observed. Since an excess of quaternary salt was apparently present in this run, the yields of methane and neopentane were lower than in runs 2 and 3. Vapor chromatographic analysis failed to show the presence of any hydrocarbons in the gaseous products of runs 1-3 except neopentane and methane. Using column "E" at 32°, 5 psi helium, the following retention times were observed: Air, 1.4 minutes; neopentane, 2.5 minutes; n-pentane, 6.5 minutes; isopentane, 4.8 minutes; 2-methyl-2-butane, 14.0 minutes. At 30° on the same column, neopentane had a retention time of 3.2 minutes; cyclopropane, 3.85 minutes; and 1,1-dimethylcyclopropane, 7.75 minutes.

Table 9. Products of the Reaction of $Me_3CCH_2NMe_3I$ with Sodium in 200 ml. of Liquid Ammonia, and Ratios of RH/CH_4

Run No.	Initial Salt mmoles	Sodium mmoles	Yields, Millimoles and Per Cent[a] CH_4 mmoles	$(CH_3)_4C \times 10^{+3}$ mmoles	Ratio $RH/CH_4 \times 10^{+3}$	Corrected Ratio $3\ RH/CH_4 \times 10^{+2}$
1	3.89	7.82	2.278±0.137 58.6%	10.60±1.13 0.27%	4.650±0.772	1.395±0.232
2	3.81	7.39	2.273±0.196 85.9%	12.37±1.24 0.32%	3.780±0.605	1.134±0.182
3	3.89	8.70	3.080±0.182 79.2%	12.63±1.28 0.33%	4.105±0.657	1.232±0.197

Average Corrected Ratio $3\ RH/CH_4$, runs 1-3 = $1.25\ (\pm 0.20) \times 10^{-2}$

[a]Yields are calculated on the basis of initial quaternary salt taken.

CHAPTER IX

DISCUSSION AND CONSLUSIONS

TH_e ratios of cleavage of higher molecular weight hydrocarbons (RH) to methane in the quaternary ammonium salts $Ph_3CCH_2NMe_3I$, $Me_3CCH_2NMe_3I$, and $Ph_3CCH_2CH_2NMe_3I$ by sodium in liquid ammonia at -33° have been determined. After correction of ratios for statistically equal numbers of R^- and CH_3^- groups on nitrogen, values of 8900 ± 1600, 0.0125 ± 0.0020 and 92 ± 16, respectively, were obtained. Grovenstein and Stevenson[8] report ratios of 0.0083 ± 0.0006, 0.0169 ± 0.0012 and 0.0089 ± 0.0029 for the cleavage of ethyl, n-propyl and n-butyl groups respectively under the same reaction conditions. It is noted that the ratios of cleavages of neopentyl, propyl, and n-butyl groups are equal, within experimental errors.

Examination of molecular models* of the three quaternary salts studied in this work show that $Ph_3CCH_2NMe_3I$ and $Me_3CCH_2NMe_3I$ possess a similar degree of steric strain, while $Ph_3CCH_2CH_2NMe_3I$, as expected, shows much less compression. N-Methyl and C-methyl hydrogens in the least strained configuration of $Me_3CCH_2NMe_3I$ are approximately 1.80 Å apart. N-Methyl hydrogens and hydrogen atoms on the aromatic rings in the least

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*The author is grateful to Dr. John R. Dyer for the use of a Dreiding Stereomodel kit (manufactured by Swissco Instrument Co., 518 S. 2nd Street, Greenville, Ill.) from which the molecular models were constructed. Atomic radii in this kit are made to scale, enabling estimation of steric interactions between atoms or groups.

strained configuration of $Ph_3CCH_2NMe_3I$ are separated by about 1.69 Å. In the higher homolog, $Ph_3CCH_2CH_2NMe_3I$, interaction of N-methyl and aromatic hydrogens is negligible (i.e., separation is greater than twice the van der Waal's radius[46] of hydrogen, 1.2 Å) although some interaction of N-methyl and α-hydrogens occurs (separation ca. 2.0 Å).

A model of the neopentyl carbanion shows it to be essentially strain free, while $Ph_3CCH_2^-$ and $Ph_3CCH_2CH_2^-$ are slightly strained to about the same extent (distances of α-hydrogens to aromatic hydrogens ca. 2.0 Å).

In view of the previously cited[8] estimation that the steric acceleration factor in the neopentyltrimethylammonium ion could be as high as 290 (if the transition state had the same steric compression as the products), it is surprising that no acceleration is observed with the neopentyl group as compared with propyl or n-butyl. However, if during the process of two-electron attack upon $Me_3CCH_2NMe_3^+$ to cleave neopentyl carbanions the transition state more closely resembles the starting material than the products, this steric acceleration effect would be diminished. Since it is evident that steric factors are relatively unimportant in accelerating cleavage, it is possible that solvent effects (especially in ammonia) tend to cancel the acceleration from steric compression in the salt. This could occur if the attempt of solvent molecules to solvate the transition state only succeeded in crowding it more. If the inductive effect of methyl groups in the neopentyl carbanion is to donate electrons, this would tend to destabilize the product. The

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46. L. Pauling, Nature of the Chemical Bond, 3rd ed., Cornell University Press, Ithaca, N. Y., 1960, p. 260.

cleavage of Me_3CCH_2- even though sterically accelerated would thus be electronically hindered.

The similarity in degree of steric strain in $Ph_3CCH_2NMe_3I$ and $Me_3CCH_2NMe_3I$ leads to either of two conclusions with regard to the high extent of $Ph_3CCH_2^-$ cleavage: First, that the transition state involved in the cleavage of $Ph_3CCH_2NMe_3^+$ resembles the products more than the reactant, allowing both steric and electronic acceleration of the large group; and second, that the transition state for the cleavage of $Me_3CCH_2NMe_3^+$ and $Ph_3CCH_2NMe_3^+$ is very similar for the two, leaving only electronic factors to account for the acceleration.

An estimate of the magnitude of the electronic acceleration of $Ph_3CCH_2^-$ cleavage from $Ph_3CCH_2NMe_3^+$ may be obtained since the cleavage ratios of $Ph_3CCH_2NMe_3^+$ and $Ph_3CCH_2CH_2NMe_3^+$ are both known and $Ph_3CCH_2CH_2NMe_3^+$ is not appreciably strained. Thus, if the decrease in inductive power of the phenyl groups through an additional methylene group can be estimated, the change in electronic acceleration between the two quaternary salts can be calculated. Branch and Calvin[47] have discussed such changes in inductive power through an equation of the form

$$\log K = A + B + C \text{ ------ } + \sum I_a \alpha^i$$

where K as originally derived refers to the ionization constant of a carboxylic acid. A, B, C------ are miscellaneous factors affecting K such as ionization constant of the solvent, steric effects, etc. The

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47. G. E. K. Branch and M. Calvin, The Theory of Organic Chemistry, Prentice-Hall, Inc., New York, 1941, pp. 203-204, 221.

final term represents inductive effects for transmission through $-CH_2-$ groups where

I_a is an inductive constant for each atom (or group) other than H

α is the fraction that reduces the inductive effect for each transmission across an atom (for carboxylic acids, and presumably any other species, $\alpha = 1/2.8 = 0.357$ according to Branch and Calvin)

i is the number of atoms separating the inducing atom (or group) from the functional group or reaction center.

The authors point out that the inductive constant I for a group is constant only when the group is substituted for a hydrogen atom in a position where it is not conjugated with another group, and when the same solvent is chosen. The use of a single value for α is restricted to a chain of atoms connected by single bonds.

If the Branch and Calvin equation is appropriate for kinetic data also, then K may be considered the ratio of cleavage of a particular alkyl group to methyl. Comparison of K values for two compounds reacting under similar conditions allows the "miscellaneous" factors to cancel, leaving an equation of the form

$$\log K_1 - \log K_2 = I_{a_1} \alpha^{i_1} - I_{a_2} \alpha^{i_2}.$$

For the cleavage of $CH_3CH_2NMe_3I$, assuming the reaction center to be on the α-carbon and comparing with the cleavage of Me_4NI,

$$\log K_{CH_3CH_2-} - \log K_{CH_3-} = I_{CH_3-} \alpha^0 - (0) = I_{CH_3-}$$

$$\log K_{CH_3CH_2-} = -2.08 = I_{CH_3-}$$

and for $Ph_3CCH_2CH_2NMe_3I$,

$$\log K_{Ph_3CCH_2CH_2-} - \log K_{CH_3CH_2-} = I_{Ph_3C-}\alpha$$

$$\log K_{Ph_3CCH_2CH_2-} = 1.96 = -2.08 + 0.357\ I_{Ph_3C-}$$

so $I_{Ph_3C-} = +11.3$

but experimentally, $\log K_{Ph_3CCH_2-} = I_{Ph_3C-} = 3.95$.

Thus, the Branch and Calvin equation indicates that the observed inductive effect of the Ph_3C- group is much greater in $Ph_3CCH_2CH_2NMe_3I$ than would be predicted. In practical terms, using the following relative rates of cleavage from quaternary nitrogen:

Ph_3CCH_2-	~ 8900
$Ph_3CCH_2CH_2-$	~ 92
CH_3-	1
CH_3CH_2-	~ 0.0083

it is seen that substitution of Ph_3C- for H- on a methyl group accelerates cleavage 8900 fold. However, substitution of Ph_3C- for H- on an ethyl group also accelerates cleavage by a factor of 11,700 fold, even though the substitution is one $-CH_2-$ group further removed from the reaction center. The data indicates qualitatively that electronic factors play a dominant role in the acceleration of cleavage. One explanation of the abnormally large acceleration of $Ph_3CCH_2CH_2-$ cleavage compared to the

predicted value is that stabilization of the carbanion through resonance occurs:

$$Ph_3CCH_2CH_2^- \longleftrightarrow Ph_3C^- \; CH_2{=}CH_2$$

thus lowering free energy of activation in going from the quaternary salt to the carbanion when compared for the $\Delta F^{\ddagger}$ required to go from $Ph_3CCH_2NMe_3I$ to $Ph_3CCH_2^-$. This type of "anionic hyperconjugation" or no-bond resonance was used by Roberts and coworkers[48] to explain the strong electron withdrawing influence of the p-trifluoromethyl group in electrophilic aromatic substitutions. No-bond resonance for $Ph_3CCH_2^-$ of the type

$$Ph_3CCH_2^- \longleftrightarrow Ph^- \; Ph_2C{=}CH_2,$$

although it is possible, is not considered as likely a possibility as that in the case of $Ph_3CCH_2CH_2^-$.

The application of the Taft equation to the data from this research leads to other interesting results.[49,50] If all steric and resonance effects are ignored, the equation takes the form

$$\log (k/k_o) = \rho^* \sigma^*$$

where σ^* is Taft's polar substituent constant

and ρ^* is the reaction constant for a given process under specific conditions.

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48. J. D. Roberts, R. L. Webb and E. A. McElhill, J. Am. Chem. Soc., 72, 408 (1950).

49. Dr. Jack Hine, private communication.

50. For discussion of the Taft equation, see R. W. Taft, Jr., in M. S. Newman (ed.), Steric Effects in Organic Chemistry, John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 590-594.

For the present work, the ratio k/k_o may be taken as the ratios of RH/CH_4 found. In order to apply the above equation, some means of estimation of σ^* must be available. Taft has listed σ^*'s for Ph-, Ph_2CH-, $PhCH_2$-, and $PhCH_2CH_2$- groups so that approximations may be made for the σ^* of Ph_3C-, Ph_3CCH_2- and $Ph_3CCH_2CH_2$-. A list of σ^* values and of log (k/k_o) values is found in Table 10. These data are shown graphically in Figure 8. It is seen that a good linear relationship exists between Ph_3CCH_2-, methyl, n-propyl and n-butyl groups. Points for ethyl and neopentyl fall to either side of the line; their deviation might be attributed to experimental error in their determination, or to some unusual aspect of their behavior. The proximity of the point for $Ph_3CCH_2CH_2$- depends on the method of calculation of σ^*. Slope of the line, ρ^*, is found to be +17.2. The value of ρ^* for ionization of carboxylic acids in water at 25° is approximately + 1.721. Using a model of the type R-X-Y-Z, in carboxylic acids the Y-Z bond is broken. In the case of quaternary salts, the R-X bond is cleaved, thus the R group is two bonds closer to the reaction center. If we apply the approximation of Branch and Calvin that intervening methylene groups decrease the inductive power of R by 2.8 fold, then ρ^* for quaternary salt cleavage is roughly $+ 1.72 (2.8)^2 = + 13.5$ for water as solvent at 25°. At a lower temperature and in a solvent of lower dielectric constant (NH_3) the reaction would be expected to be more selective and more dependent on the inductive effects of substituted groups, leading to a higher value of ρ^*.[51] This indicates that the application of the Taft relationship to the data from this work is at least reasonably valid.

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51. H. H. Jaffé, Chem. Revs., 53, no. 2, 195-219 (1953).

Table 10. Values of Taft Polar Substituent Constants[50] and log (k/k_o)

Group	σ^*	log (k/k_o) = log (RH/CH_4)
Ph_3C	+0.60[a]	---
Ph_2CH	+0.405	---
Ph_3CCH_2	+0.215[b]	+3.95
$PhCH_2$	+0.215	---
$Ph(CH_3)CH$	+0.105	---
$PhCH_2CH_2$	+0.08	---
$Ph_3CCH_2CH_2$	(+0.08)[c]; (-0.02)[d]	+1.96
CH_3	0.000	0.000
CH_3CH_2	-0.10	-2.08
n-C_3H_7	-0.115	-1.78
n-C_4H_9	-0.130	-2.05
neo-C_5H_{11}	-0.165	-1.90

[a]Estimated from the effect of adding Ph- groups to CH_3-, an increase of approximately + 0.20 per addition.

[b]Estimated by the addition of a Ph_3C- group to CH_3-, then reducing its inductive effect 2.8 fold.

[c]Estimated by reducing the value of Ph_3CCH_2 by 2.8 fold.

[d]Estimated by the addition of a CH_3- group to CH_3-, then adding a Ph_3C- group whose inductive constant has been reduced by $(2.8)^2$ fold.

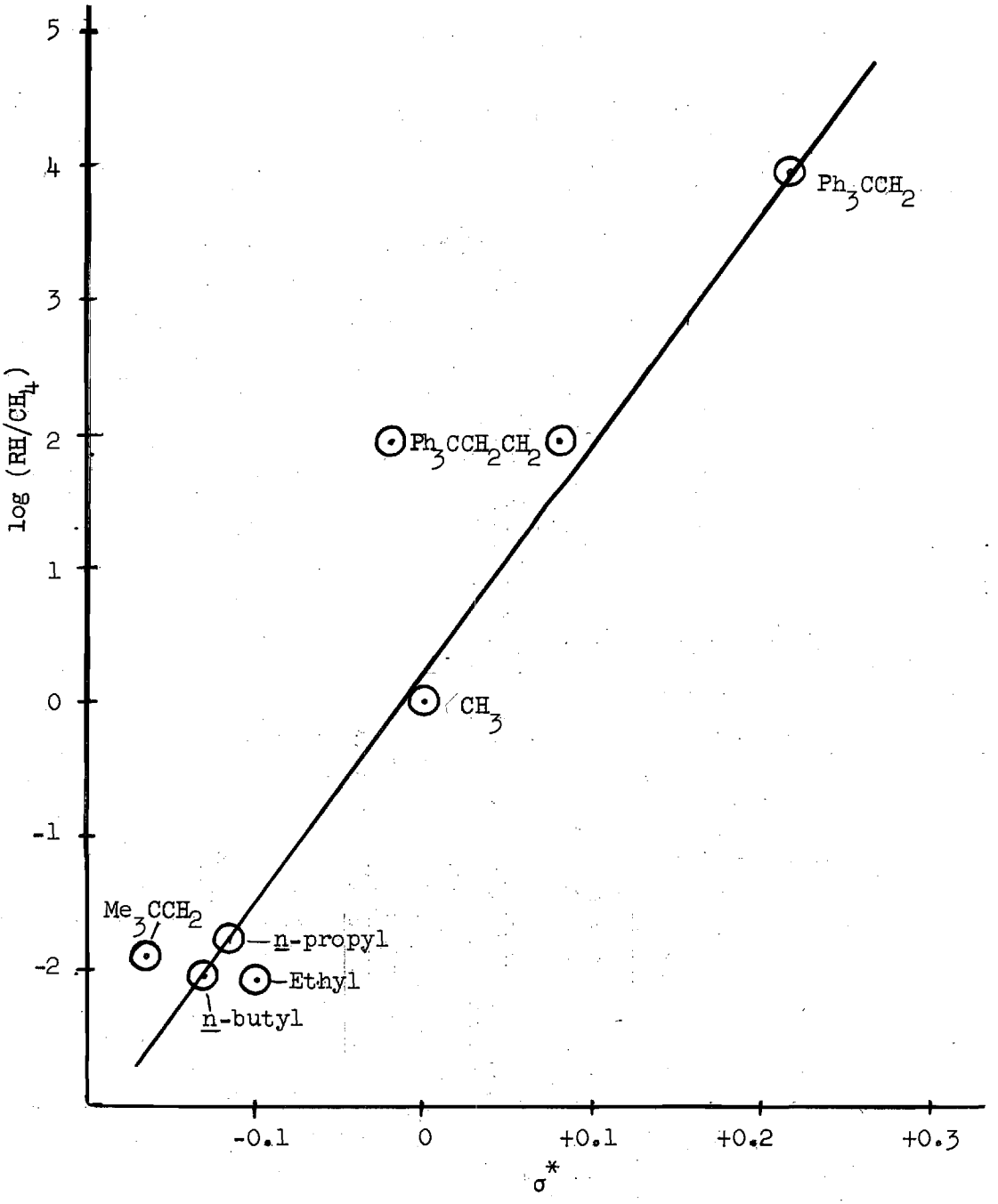

Figure 8. Plot of log (RH/CH_4) vs. Taft's σ^* for Various R groups.

The cleavage of quaternary ammonium salts by sodium in liquid ammonia in the presence of an acid such as ammonium chloride helps to give an indication of the nature of the reduction. Data on the reaction of $Ph_3CCH_2NMe_3I$ with sodium and NH_4Cl indicate that little or no change in the ratio RH/CH_4 occurs over that observed in the absence of NH_4Cl. This is of necessity a qualitative statement since the irregularities in the data from runs in the presence of NH_4Cl were such that only a three-fold or greater change in the RH/CH_4 ratio would have been noticed. Reactions of $Ph_3CCH_2CH_2NMe_3I$ with sodium in the presence of NH_4Cl failed to give any useful information as to the effect of acid on the RH/CH_4 ratio since the reaction of sodium with ammonium chloride is much faster than with the quaternary salt. Very low yields of cleavage products (ca. 10 per cent based on starting salt) resulted and gaseous hydrocarbons were diluted with hydrogen to the point where accurate analysis by vpc was impossible. The absence of any large effects of NH_4Cl on $Ph_3CCH_2NMe_3I$ cleavage indicates that the reaction is a heterogeneous one; i.e., reaction takes place close to the surface of the solid sodium in such a way that NH_4^+ ions are unable to interfere. This may be due to the fact that the NH_4Cl is consumed by sodium before it can approach the reaction site of $Ph_3CCH_2N(CH_3)_3I$.

It has been shown also that in the presence of NH_4Cl, the extent to rearrangement of the carbanion intermediate $Ph_3CCH_2^-$ is not appreciably changed from cleavage in absence of NH_4Cl. This fact has much significance in that it shows that the Ph_2CHCH_2Ph produced in the reaction of $Ph_3CCH_2NMe_3I$ with sodium in liquid ammonia does not likely arise from reduction of $Ph_2C{=}CHPh$. The presence of excess NH_4Cl in a reaction mixture

would keep the concentration of NH_2^- or carbanion so low as to prevent significant elimination of $Ph_2C{=}CHPh$ from $Ph_3CCH_2NMe_3I$. The formation of rearranged product in the presence of NH_4Cl could indicate that rearrangement can occur simultaneously with cleavage. Another possibility, however, is that the carbanions $Ph_3CCH_2^-$ and $Ph_2\ddot{C}\text{-}CH_2Ph$ extract a proton from NH_3 about as readily as from NH_4^+.

The cleavage of $Ph_3CCH_2NMe_3I$ with sodium in dioxane at reflux gave a ratio of hydrocarbons to methane of 9 or less, after correction for unrecovered gaseous products. This is a surprising result, since Grovenstein and coworkers[8,52] in earlier experiments have reported that cleavages in dioxane at reflux were less selective, but not to such a great extent. For instance, the propane to methane ratio for $CH_3CH_2CH_2NMe_3^+$ changes from 0.0169 in ammonia at -33° to 0.024 in dioxane at 99°. The drop in RH/CH_4 ratio from 8900 in ammonia to 9 in dioxane indicates a great change in the nature of the transition state, or perhaps in the mechanism of cleavage. The absence of a red or green color in the reaction mixture cannot be explained. Grovenstein[11] observed an intense red in the reaction of Ph_3CCH_2Cl with sodium in dioxane. He also found that triphenylethylene is very rapidly reduced to 1,1,2-triphenylethane with sodium in dioxane at reflux under the same conditions as used in the present work to give a dark green carbanion. It is, therefore, an apparent anomaly that more than twice as much unreduced $Ph_2C{=}CHPh$ (11.95 per cent) as Ph_2CHCH_2Ph (4.84 per cent) was isolated from the reaction mixture, even though an excess of sodium metal was present. Also, of the saturated hydrocarbons

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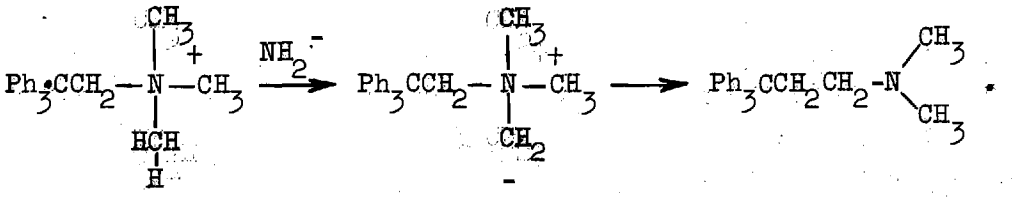
52. E. Grovenstein, Jr., E. P. Blanchard, Jr., D. A. Gordon, and R. W. Stevenson, J. Am. Chem. Soc., 81, 4842 (1959).

corresponding to cleavage products, 18 per cent were products expected from rearrangement. One explanation for these observations is that two processes were occurring at the same time: the $Ph_3CCH_2NMe_3I$ was being cleaved to $Ph_3CCH_2^-$ which either rearranged or abstracted a proton from additional quaternary salt to give the α-elimination product $Ph_2C{=}CHPh$. Elimination of triphenylethylene from $Ph_3CCH_2NMe_3I$ is accelerated either by the increase in temperature or increase in base strength since with $NaNH_2$ or KNH_2 in liquid ammonia, very little olefin is found. Although no $Ph_3CCH_2CH_2N(CH_3)_2$ was isolated from dioxane, the $Ph_3CCH_3N(CH_3)_2$ initially isolated was impure and may have contained some of the higher homolog. A nucleophilic attack upon $Ph_3CCH_2NMe_3^+$ at high temperature by I^- or other species to give $Ph_3CCH_2NMe_2$ is a possible explanation for the high yield of amine in dioxane.

In liquid ammonia, $NaNH_2$ or KNH_2 acting on $Ph_3CCH_2NMe_3I$ gives rise to the amine $Ph_3CCH_2CH_2NMe_2$. Higher yields arise from KNH_2, presumably due to its higher solubility in the solvent. The formation of this amine is proposed to arise through a type of Stevens rearrangement, with migration of the Ph_3CCH_2 group:



A rearrangement of this type is of considerable interest, since migration of such bulky groups is uncommon in the Stevens rearrangement.[53]

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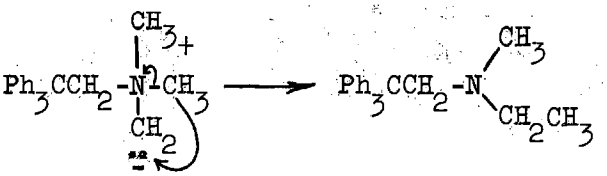
53. C. K. Ingold, op. cit., pp. 524-527.

The presence of electron withdrawing groups tends to reduce the S_N2 reactivity of a molecule,[54] but increases the ability of a group to migrate in an internal rearrangement.[53] The rearrangement as observed may be explained in terms of three factors: first, considerable strain would be relieved in going from the quaternary salt to the amine $Ph_3CCH_2CH_2NMe_2$; second, the amine formed from methyl migration, $Ph_3C-\underset{\underset{CH_3}{|}}{CH}-NMe_2$ would exhibit almost as much strain as the starting salt and certainly more strain than $Ph_3CCH_2CH_2NMe_2$; and third, the amine formed from the migration



would be almost as strained as the starting quaternary salt $Ph_3CCH_2NMe_3I$ since most of the compression and strain result from interaction of N-methyl hydrogens and the aromatic rings. With an ethyl group in place of methyl on nitrogen, assuming retention of a tetrahedral configuration about nitrogen, interaction with the rings would be expected to remain almost as great in the tertiary amine as for the salt $Ph_3CCH_2NMe_3I$.

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54. J. Hine, Physical Organic Chemistry, 2nd ed., McGraw-Hill, Inc., New York, N. Y., 1962, p. 175.

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BIOGRAPHICAL SKETCH

Lynn Calloway Rogers was born April 15, 1939, in Oklahoma City, Oklahoma, to Harold L. and Emmagene Rogers. From 1941, he resided in Maysville, Oklahoma and attended public schools until his graduation from Maysville High School as salutatorian in June, 1956. He entered the University of Oklahoma in September of 1956, completed requirements for graduation in November, 1960, and received the degree Bachelor of Science in Chemistry in June, 1961.

The author entered the graduate school of the Georgia Institute of Technology in September of 1960 and completed requirements for the degree Master of Science in Chemistry in August, 1962. While at Georgia Tech, the author held a Research Assistantship under a grant from the Petroleum Research Fund of the American Chemical Society. He is a member of Alpha Chi Sigma and Phi Lambda Upsilon fraternities and the American Chemical Society.

On June 6, 1959, he married the former Gwendolyn Forkner of Lindsay, Oklahoma, and to this union on January 22, 1961, was born a son, Randall Lynn, in Atlanta, Georgia. He has accepted employment with the Continental Oil Company at Ponca City, Oklahoma.